PB85-216562

Evaluation of New and Emerging Technologies in the Metal Finishing Industry

University of Central Florida, Orlando

Prepared for

Environmental Protection Agency, Cincinnati, OH

Jun 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-216562

EPA/600/2-85/072
June 1985

EVALUATION OF NEW AND EMERGING TECHNOLOGIES IN THE METAL FINISHING INDUSTRY

by

John D. Dietz and Christopher M. Cherniak
University of Central Florida
Orlando, Florida 32816

CR-810787-01-0

Project Officer

M. Lynn Apel
Industrial Wastes and Toxics Technology
Water Engineering Research Laboratory
Cincinnati, Ohio 45268

This study was conducted in cooperation with
the Research Board of
The American Electroplaters' Society, Inc.
AES Project 63

WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-85/072	2.
3. RECIPIENT'S ACCESSION NO. PB85-216562	
4. TITLE AND SUBTITLE Evaluation of New and Emerging Technologies in the Metal Finishing Industry	5. REPORT DATE June 1985
	6. PERFORMING ORGANIZATION CODE US EPA/WERL/IWTTD
7. AUTHOR(S) J.D. Dietz and C.M. Cherniak	8. PERFORMING ORGANIZATION REPORT NO. Project No. 01198
9. PERFORMING ORGANIZATION NAME AND ADDRESS College of Engineering University of Central Florida P.O. Box 25,000 Orlando, FL 32816	10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. CR-810787-01
12. SPONSORING AGENCY NAME AND ADDRESS Water Engineering Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Final Report 5/83-12/84 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES
Research was performed in cooperation with the American Electroplater's Society, Orlando, FL (AES Project 63) M. Lynn Apel, Project Officer, 513-684-7502

16. ABSTRACT

A research program was completed to identify new and emerging waste management technologies in the metal finishing industry. A limited field sampling and analytical program was pursued to define performance at full scale operating facilities for the following technologies: 1)buoyant media filtration - 3M; 2) Zerpol zero liquid discharge; and 3) Zerpa distillation solvent recovery.

Information was developed regarding cost, performance, safety, and applicability of these technologies. A preliminary evaluation of the processes based on the limited testing indicated potential applications of all three processes in segments of the metal finishing industry.

This report was submitted in fulfillment of cooperative agreement CR-810787-01-0 by The Americal Electroplaters' Society, Inc. under the partial sponsorship of the U.S. Environmental Protection Agency. The work was performed via subcontract to the University of Central Florida, Civil Engineering and Environmental Sciences Department. This report covers period from May 18, 1983 to August 17, 1984, and work was completed as of December 14, 1984.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Metal Finishing Electroplating Emerging Technologies Wastewater Solid Waste	Filtration Zero Discharge Solvent Recovery Metals Removal Metal Recovery	

18. DISTRIBUTION STATEMENT Unrestricted: Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 99
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded in part by the United States Environmental Protection Agency under cooperative agreement CR-810787-01-0 to The American Electroplaters' Society, Inc. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report summarizes information on three emerging technologies for management of wastes in the metal finishing industry. The reported data were obtained through limited sampling and analysis of operating systems. This preliminary evaluation of performance and economics was completed to provide information to affected segments of the metal finishing industry, including plant owners and operators, engineers, consultants and regulatory officials.

Further information concerning this subject may be requested from the Industrial Wastes and Toxics Technology Division of the Water Engineering Research Laboratory.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

A research program was completed to identify new and emerging waste management technologies in the metal finishing industry. A limited field sampling and analytical program was pursued to define performance at full scale operating facilities for the following technologies:

1. Buoyant media filtration - 3M
2. Zerpol® zero liquid discharge
3. Zerpa distillation solvent recovery

Information was developed regarding cost, performance, safety, and applicability of these technologies. A preliminary evaluation of the processes based on the limited testing indicated potential applications of all three processes in segments of the metal finishing industry.

This report was submitted in fulfillment of cooperative agreement CR-810787-01-0 by The American Electroplaters' Society, Inc. under the partial sponsorship of the U.S. Environmental Protection Agency. The work was performed via subcontract to the University of Central Florida, Civil Engineering and Environmental Sciences Department. This report covers a period from May 18, 1983 to August 17, 1984, and work was completed as of December 14, 1984.

CONTENTS

Foreword iii
Abstract v
Figures ix
Tables x
Acknowledgment xi

1. Introduction. 1
2. Conclusions 5
3. Recommendations 7
4. Survey of Technologies. 8
5. Buoyant Media Filtration. 13
    Process Description. 13
    Application at 3M Facility 15
    Sampling Program 18
        Objectives. 18
        Sample Location and Frequency 18
        Analytical Program 19
        Results 20
    Evaluation of Process. 26
6. Zerpol® Zero Liquid Discharge 29
    Process Description. 29
        System Configuration. 30
        Zerpol® Applications Surveyed in this Program 32
            Pioneer Metal Finishing-Franklinville, NJ . . . 32
            Plate-Rite Company, Folcroft, PA 34
            James Spring and Wire Company - Frazer, PA . . . 36
    Sampling Program 41
        Objectives 41
        Sample Location and Frequency 42

CONTENTS (continued)

Analytical Program. 43
Results 43
Discussion of Operating Experience 47
Evaluation of Process. 48
7. Zerpa - Distillation Solvent Recovery 55
Process Description. 55
Application at W. A. Parsons Company-Durham, CT. 56
Sampling Program 58
Objectives. 58
Sample Location and Frequency 58
Analytical Program. 58
Results 58
Evaluation of Process. 59

References 64
Appendices 66

A. Advertisement of Project 66
B. Quality Assurance Considerations 67
C. Statistical Procedures 76
D. Photographs of Facilities. 79

FIGURES

Number		Page
1.	Worth-assessment model.	10
2.	Buoyant media filter schematic.	14
3.	Process flowsheet - buoyant media filtration.	17
4.	Zerpol® zero liquid discharge schematic	31
5.	Process flowsheet - Pioneer Metal Finishing	35
6.	Process flowsheet - Plate-Rite Company.	39
7.	Process flowsheet - James Spring and Wire Company	40
8.	Process flowsheet - distillation solvent recovery	57

TABLES

Number		Page
1.	Effluent Limitations.	2
2.	Data Bases Examined for Literature Search	8
3.	Metal Finishing Operations - 3M Company	16
4.	Clarifier Performance - Composite Samples	21
5.	Buoyant Media Filter Performance - Composite Samples.	22
6.	Statistical Summary of Grab Sample Data	24
7.	Dynamic Response Summary.	25
8.	Buoyant Media Filter Capital Cost Estimate.	27
9.	Plating Line Configuration - Pioneer Metal Finishing.	33
10.	Plating Bath Solutions - Pioneer Metal Finishing.	34
11.	Plating Line Characterization - Plate-Rite Company.	37
12.	Plating Bath Solutions - Plate-Rite Company	38
13.	Plating Bath Solutions - James Spring and Wire Company.	41
14.	Zerpol® Zero Liquid Discharge - Pioneer Metal Finishing Composite Samples	44
15.	Zerpol® Zero Liquid Discharge - Plate-Rite Company - Composite Samples	44
16.	Zerpol® Zero Liquid Discharge - James Spring and Wire Company Composite Samples	45
17.	Zerpol® Zero Liquid Discharge - Pioneer Metal Finishing - Influent Grab Samples	45
18.	Zerpol® Zero Liquid Discharge - Pioneer Metal Finishing - Condensate Grab Samples	46
19.	Zerpol® Zero Liquid Discharge - Annual Cost Summary	49
20.	Characterization of Recovered Solvent Blend	59
21.	Capital Cost Estimates - Zerpa Solvent Recovery	61
22.	Operating Cost Summary - Zerpa Solvent Recovery	61
23.	Payback Period - Zerpa Solvent Recovery Installations	61

ACKNOWLEDGMENT

The authors gratefully acknowledge the technical support received on this project from Dr. Rebecca M. Spearot of the AES Research Board and Dr. Clarence H. Roy of the AES Environmental Committee.

SECTION 1

INTRODUCTION

PROJECT OBJECTIVES

Enactment of federal legislation over the preceding decade has resulted in the implementation of extensive pollution management programs in the electroplating and metal finishing industry. Final regulations which govern the liquid effluent discharge from these operations were recently adopted. As published in the Federal Register (40 CFR Parts 413 and 433) on July 15, 1983 (1), effluent limitations guidelines and pretreatment standards have been established for a number of toxic metals (Cd, Cr, Cu, Pb, Ni, Ag, Zn), cyanide, total toxic organics (TTO), oil and grease, total suspended solids (TSS), and pH.

The effluent limits reported in Table 1 are based on end-of-pipe performance achieved by chemical precipitation and clarification, and preliminary treatment, where necessary, consisting of cyanide destruction, hexavalent chromium reduction, and oil and grease removal.

Although the effluent standards are based on application of a specific technology, the individual discharger has the option to select an alternative method of treatment. New processes for treatment of metal finishing wastes and/or recovery of valuable wastewater components have been developed in response to the environmental legislation and regulations of the preceding decade. The U. S. Environmental Protection Agency (EPA) and The American Electroplaters' Society, Inc. (AES) have been involved in many studies to define the performance of promising techniques and to distribute the information to the affected segments of the metal finishing industry. These technologies offer great environmental benefits by improving existing processes and industry's ability to meet applicable standards while minimizing adverse economic impacts. This project represented a continuation of

the cooperative effort between EPA and the AES to define and evaluate new and emerging technologies for wastewater management in the metal finishing industry.

TABLE 1. EFFLUENT LIMITATIONS

Pollutant or Pollutant property	Maximum for any 1 day	Monthly average shall not exceed
Cadmium, mg/L	0.69	0.26
Chromium, mg/L	2.77	1.71
Copper, mg/L	3.38	2.07
Lead, mg/L	0.69	0.43
Nickel, mg/L	3.98	2.38
Silver, mg/L	0.43	0.24
Zinc, mg/L	2.61	1.48
Cyanide, mg/L	1.20	0.65
TTO, mg/L	2.13	--
Oil and Grease, mg/L	52	26
TSS, mg/L	60	31
pH	within 6.0 to 9.0	within 6.0 to 9.0

The principal objectives of the research program were to identify and evaluate in a preliminary manner new technologies for the management of wastes in the metal finishing industry. Attention was directed toward methodologies with potential application to the treatment of industrial liquid effluent and residual solvent and solids streams to evaluate the effectiveness and potential of the "emerging" technology for applicability on an industry-wide scale.

For the purposes of this research effort, new and emerging technologies were defined as those technologies which represented an alternative method for wastewater treatment to the conventional chemical precipitation and clarification practice. In some cases, the technologies incorporated a novel modification to a component of a conventional precipitation process;

thus it was not mandatory that the candidate technologies involve total absence of the chemical precipitation method for treatment.

In order to be eligible for consideration in this study, it was also necessary that the technology represent a very specific stage of development. The central effort of the research program involved sampling and analysis of an existing facility in operation. Therefore, it was mandatory that the process be completely developed to a prototype stage. This requirement eliminated treatment methods from consideration which were not advanced beyond a conceptual stage.

At the other end of the spectrum, there was no interest in characterization of a process which had been successfully demonstrated in widespread use for a period of years. The objectives of the study were to develop information for new processes to facilitate distribution of information to affected segments of the metal finishing community. The processes could involve technology transfer of current practices from alternate industrial applications.

PROJECT HISTORY

The research program was initiated in May 1983 with an aggressive effort to solicit information regarding new technologies from the metal finishing industry. Based on information received through September 1983, the various candidate technologies were evaluated to select a limited number for detailed characterization via field sampling and analysis. Three technologies were selected for on-site characterization:

1. Buoyant media filtration - 3M
2. Zero liquid discharge - Zerpol®
3. Distillation solvent recovery - Zerpa

The field sampling activities were completed in April and May, 1984. The results of the sampling and analytical program are presented in this final report.

ORGANIZATION OF REPORT

The organization of this report generally parallels the project sequence of activities. The initial phase of work involved acquisition of information for identification and evaluation of potential technologies. These efforts are described in Section 4, which also includes a description of the model which was employed for selection of specific technologies for field characterization.

An extended discussion of the three selected technologies is provided based on information developed via on-site investigation. A detailed description of the process is presented, including a discussion of the plating and metal finishing operations encountered at each installation. Sampling activities are fully described with associated analytical results. A summary evaluation of the technology is provided based on the results of the field survey.

SECTION 2

CONCLUSIONS

Characterization of three new technologies for management of wastes in the metal finishing industry was completed via a limited field sampling and analysis program. The study objectives were confined to a preliminary evaluation of the technologies. Evaluation of the processes in the specific application selected for study may not provide sufficient information to assess applicability in all segments of the industry, although the information developed through this type of program provides a starting point for general evaluation of any new or emerging technology.

A buoyant media filtration system developed by 3M was demonstrated to achieve compliance with federal effluent guidelines when applied in place of a clarifier. The test system was subjected to significant hydraulic and solids loading fluctuations, and the buoyant media filter evidenced improved stability of operation when compared to a slant-tube clarifier. Alteration of conventional clarification systems to provide a buoyant media filter appears to be generally feasible, in which case the applicability of the process would be very significant.

Three facilities were surveyed which have successfully achieved zero liquid discharge for a period in excess of three years using the Zerpol® process. Reuse of treated effluent and condensate as rinsewater make-up did not produce problems with product quality for the chemical conditions and plating operations identified in this report. Prior operational difficulties with the boiler were reported if certain cleaners were used. Consequently, adoption of the Zerpol® process may limit flexibility in selection of chemicals in various plating and cleaning solutions. The rinsewater quality was characterized for the three facilities surveyed. Evaluation of the suitability of these streams for rinsewater make-up must be evaluated on a case-by-case basis for each rinsing operation.

Successful operation of a solvent recovery system for a blend of toluol, butanol, cellosolve acetate, and VM&P naphtha was documented using a Zerpa batch distillation unit. The reclaimed solvent was acceptable as a substitute for the virgin solvent blend. The operating costs for this application were determined to be $1.28 per gallon, including energy, labor, materials, and residual solids disposal. Amortization of capital costs were dependent on the volume of recovery operations. For valuable solvents, these recovery costs were very attractive.

SECTION 3

RECOMMENDATIONS

The criteria which were established for selection of technologies restricted consideration to those processes which were recently developed. This time factor precluded examination of long-term operating data for evaluation of life cycle costs and specific long-term operating problems. This general limitation applies to all three technologies which were investigated.

With respect to the buoyant media filtration system, extended studies to evaluate media durability, alternate media particle size distribution, and alternate backwash operation practices (frequency, duration, hydraulic loading) would be beneficial to enhance system development.

Development of a complete material and energy balance for the Zerpol® process would require an extended presence. A detailed examination would be beneficial to identify energy requirements for boiler operation throughout summer and winter periods. Full characterization of boiler function and associated condensate water quality cannot be established on the basis of the limited sampling effort involved in this study. Completion of a material balance would also require consideration of sludge and salts production over a compositing period which corresponds with the duration of characterization of the influent and reuse stream.

Long-term operating data would be required to assess maintenance and repair costs for the Zerpa distillation unit. Such data were not readily available due to the short history of operation.

SECTION 4

SURVEY OF TECHNOLOGIES

DEVELOPMENT OF DATA BASE

A manual and computer literature search was undertaken to identify potential technologies for consideration. Data bases searched are noted in Table 2.

TABLE 2. DATA BASES EXAMINED FOR LITERATURE SEARCH

Water Resources Abstracts, 1968-present, 161,000 records, monthly updates (U.S. Department of the Interior, Washington, DC).
METADEX (Metals Abstracts/Alloys Index), 1966-present (Alloys Index, 1974-present), 497,000 records, monthly updates (American Society for Metals, Metals Park, OH).
Comprehensive Dissertation Index, 1861-present, 801,000 records, monthly updates, (University Microfilms International, Ann Arbor, MI).
Conference Papers Index, 1973-present, 944,000 records, monthly updates, (Cambridge Scientific Abstracts, Bethesda, MD).

The search was restricted to the years 1980 to 1983 to limit the quantity of material consistent with the intention to identify "new" technologies.

A descriptive notice was placed in the following publications in an attempt to solicit information directly from manufacturers, developers, vendors, inventors, and users: Plating and Surface Finishing, Products Finishing, Industrial Finishing, Metal Finishing, Journal of the Water Pollution Control Federation, Environmental Science and Technology, and Water and Wastes Digest. A sample display advertisement is included in Appendix A. Follow-up telephone calls were used to contact individuals identified through the advertising campaign. The response was significant,

with over 30 contacts initiated based on the notices published in these journals.

A number of other publications (e.g., Hazardous Waste News) offered a brief description of the research project, presumably based on examination of the published notices. A descriptive article regarding the project objectives also was published in the September 1983, issue of Plating and Surface Finishing (2).

DEVELOPMENT AND CHARACTERIZATION OF WORTH-ASSESSMENT MODEL

A worth assessment model was developed with similar criteria to that employed in a similar EPA study (3). The model is detailed in Figure 1.

The technical merit of each technology was evaluated with respect to the following criteria: energy requirements, capital and O&M costs, degree of applicability, performance, and safety. The energy requirements, costs, and performance were evaluated on the basis of information supplied by the industry prior to any on-site examination of the technology. In this context, the performance of a candidate technology was evaluated with respect to compliance with effluent guidelines. The applicability of any technology was assessed relative to potential for modification of current systems as well as for development in new manufacturing operations. Safety concerns included occupational risks and public health effects associated with release of toxic materials into the environment.

The scoring system for these criteria was predicated on comparison to a conventional process (precipitation and clarification). Cost factors were particularly difficult to evaluate on a general basis, due to varying costs for disposal of the toxic chemical sludges in different locations in the United States. Considerations in the evaluation of costs included chemical purchase, labor, sludge disposal, power, and capital.

The success of this research effort depended on many factors which were independent of the technical merit of the candidate technologies. In order to develop meaningful data, it was necessary that the technology be developed to a sufficient degree to locate a prototype unit in an actual production facility. Consideration of technologies was restricted to those systems

CRITERIA	SCORE	WEIGHTING FACTOR
TECHNICAL MERIT		(0.05)
Energy Requirements		
Significantly less	(1.0)	
Slightly less	(0.8)	
Same as conventional	(0.5)	
Slightly more	(0.4)	
Significantly more	(0.1)	
Cost of Technology		(0.1)
Significantly less	(1.0)	
Slightly less	(0.8)	
Same as conventional	(0.5)	
Slightly more	(0.2)	
Significantly more	(0.0)	
Degree of Applicability		(0.1)
Widespread	(1.0)	
Limited	(0.5)	
Small	(0.1)	
Anticipated Performance		(0.1)
Significantly better	(1.0)	
Slightly better	(0.8)	
Same as conventional	(0.5)	
Worse than conventional	(0.1)	
Safety Considerations		(0.05)
Beneficial	(1.0)	
Same as conventional	(0.8)	
Deleterious, but solvable	(0.2)	
Very hazardous	(0.0)	
TECHNICAL PROBABILITY OF SUCCESS		
Current Level of Demonstration		(0.3)
Full-scale application	(1.0)	
Pilot-plant success	(1.0)	
Lab-scale success	(1.0)	
Literature citation only	(0.0)	
Concept only	(0.0)	
Technical Barriers		(0.1)
None	(1.0)	
Minor	(0.5)	
Serious	(0.1)	
Legal Constraints		(0.1)
None	(1.0)	
Solvable	(0.5)	
Serious	(0.1)	
COST OF SAMPLING AND ANALYSIS PROGRAM		(0.1)
Low	(1.0)	
Moderate	(0.8)	
High	(0.5)	

Figure 1. Worth-assessment model

which were already in operation or could be placed in operation in an electroplating or metal finishing facility as of October 1983.

Sufficient data from historical operating records were required to establish a basis for application of the worth-assessment model. Such data were considered to be representative if developed by full-scale, pilot-scale, or lab-scale demonstration.

Resolution of technical barriers and legal constraints which interfered with access to facilities or records could have been a lengthy process. Technical barriers involved site-specific factors relative to access for sample collection, non-representative production conditions, or non-representative performance of the identified technology. Release of information was essential in order to apply the worth-assessment model. Full cooperation with requirements for publication of the results was also essential for participation in the research program. A technology was determined to have no technical barriers or legal constraints for the purposes of this study if a field installation was available for sampling.

The final factor which was included in the worth-assessment model addressed the costs associated with completion of the sampling and analytical program.

Determination of eligibility for participation in the field characterization phase of the research centered on the criteria which were used to define "new" and "emerging" technologies. Well-established technologies were, therefore, precluded from this analysis. The requirement for completion of field sampling and analysis at an operating metal finishing facility eliminated additional technologies which were not sufficiently developed to locate full-scale or pilot-scale treatment systems. The decision to restrict consideration to new and emerging technologies at a specific stage of development was consistent with the objectives and requirements of this research program. It is emphasized that elimination of a technology from consideration did not reflect or imply any adverse judgment regarding the merit of the technology.

Based on application of the worth-assessment model, three technologies were identified which were believed to offer the greatest potential:

1. Buoyant media filtration - 3M
2. Zero liquid discharge - Zerpol®
3. Distillation solvent recovery - Zerpa

Further characterization of these three processes by on-site sampling and analysis was pursued.

SECTION 5

BUOYANT MEDIA FILTRATION

PROCESS DESCRIPTION

Buoyant media filtration refers to a granular bed filtration process in which liquid passes in an upflow mode through a media which has a density less than the filtrate. The media is held in place just below the liquid surface by a retaining screen. Backwash of the filter is achieved by reversal of the flow and subsequent fluidization of the media. This flow reversal is easily achieved by gravity withdrawal of fluid from the bottom of the filter unit. A schematic diagram of the filter unit is presented in Figure 2.

The buoyant filter media utilized in this study is manufactured by 3M Company. The media, known as 3M Brand Macrospheres, are very small, hollow beads. The shell of these beads consists of hollow glass spheres held together with a phenolic resin binder. Macrospheres are available in diameters ranging from 0.3 mm to 6 mm; mixtures of any size range and effective size can be obtained. The surface of the Macrospheres is very rough in comparison to alternative filter media (sand).

The durability of the filter media was assessed in the laboratory by 3M researchers. Studies were completed to evaluate resistance to abrasion, tolerance of pH extremes (2 to 12), chemical stability in the presence of high chlorine doses (1 percent by weight), and deterioration associated with repeated freeze-thaw cycles. Based on the results of these laboratory-scale tests, media loss was reported to be insignificant. In the absence of full-scale operating data over a prolonged period, reliance on these laboratory results is the only basis for assessment of the media durability.

The potential applications of the technology include: effluent polishing following conventional clarification, replacement of conventional

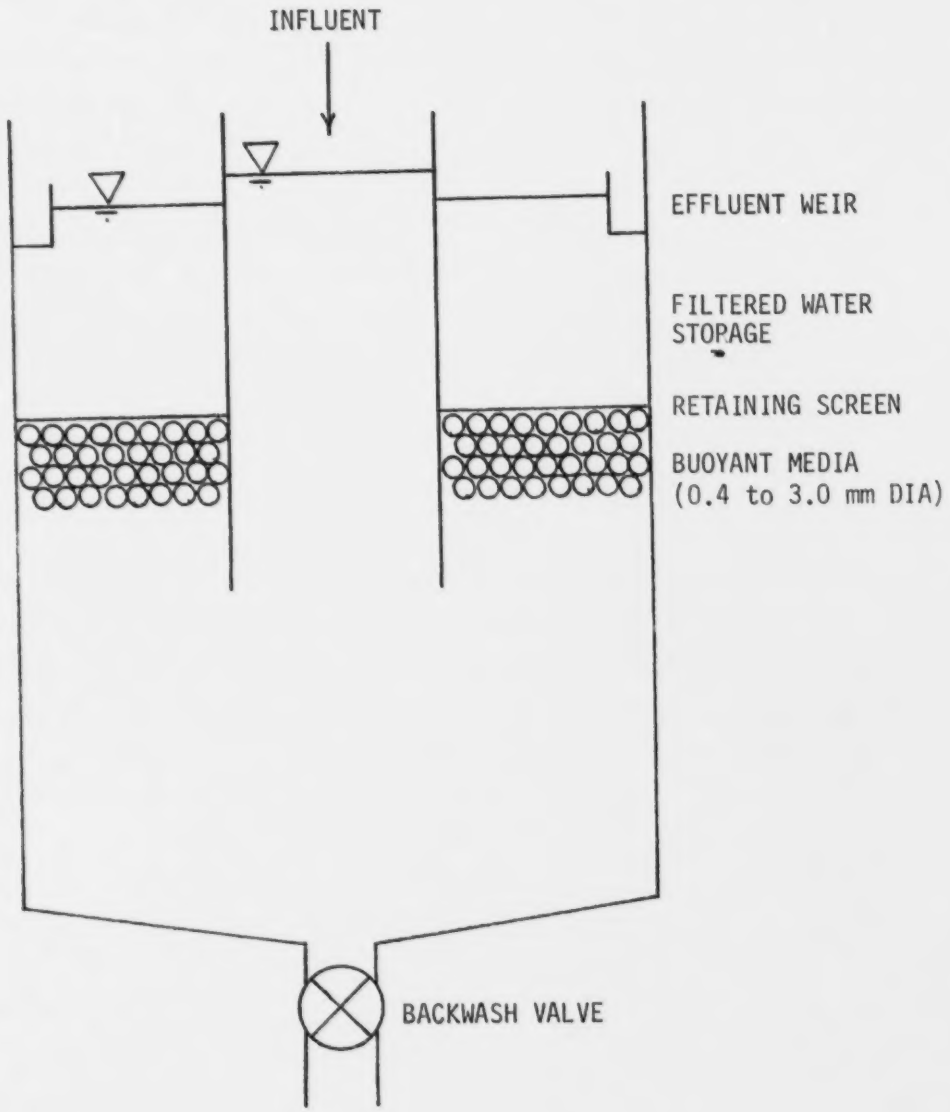

Figure 2. Buoyant media filter schematic.

clarification, and modification of conventional clarification to include a buoyant media filter at the surface of an existing clarifier.

Operation and control of the filter unit is quite simple in comparison to standard sand filtration systems due to the single valve which controls the process. Initiation of a backwash cycle can be keyed to measurement of head loss across the media, product water volume, product water turbidity, or elapsed time. Automation of the operation does not appear to present any difficulty.

Although practiced at this installation, it is not necessary to suspend feed of influent wastewater during the backwash cycle. The rapid rate of withdrawal of liquid during backwash results in a lowered water surface elevation during the backwash operation. Consequently, there is no discharge of effluent during the backwash operation.

Unlike conventional filtration systems, a separate structure for backwash source water storage is not necessary. A holding tank for the backwash stream was provided in this installation. Due to the minimal duration of the backwash cycle (about one minute), relatively small quantities of backwash water were sufficient. This water was readily available as storage in the region of the filter above the media between the retaining screen and the effluent weir (see Figure 2). The backwash stream was diverted to a holding tank, with subsequent return to a preceding process in the treatment system via pumping from an intake at the base of the backwash holding tank.

APPLICATION AT 3M FACILITY

One full-scale buoyant media filter was in operation at a 3M production facility. The filter has been in operation periodically since 1983. The original treatment system was installed without the filter, and operation of the filter has been pursued for several extended periods as a demonstration of the technology. The metal finishing operations at this plant consist of three production lines described in Table 3.

Despite flow equalization, the influent composition and flow were quite variable due to the frequent batch discharges of solutions from the production lines. It should also be noted that concurrent operation of all three production lines was not common. Suspension of operation between shifts was

TABLE 3. METAL FINISHING OPERATIONS--3M COMPANY

Process Description	Batch Dumps of Spent Solutions	Rinsewater Flowrate (gpm)	Contaminants
Batch mechanical zinc plating of steel parts with post chromating	Dumped following plating of each batch of metal parts	30	Cr^{6+}, Cr^{3+}, Zn^{2+}
Alkaline cleaning of steel parts followed by conversion coating by zinc phosphating	Spent alkaline cleaner and zinc phosphating solution are dumped frequently	10	PO_4, Alkaline Cleaner, Zn^{2+}
Electroplating tin onto copper parts	Plating solution is rarely dumped	15	Sn^{2+}, Sn^{4+}, Cu^{2+}

routinely practiced, so that intermittent flows to the waste treatment facilities were experienced.

A process flow schematic for the waste treatment process is presented as Figure 3. The treatment system components include:

1. Equalization
2. Pumping (60 gpm)
3. Chromium Reduction - Set Point pH = 2.5 (feedback control)
   - Set Point ORP= 280 mV (feedback control)
4. Neutralization-precipitation - Set Point pH=9.0 (feedback control)
5. Flocculation - polymer addition (American Colloid 727)
6. Sedimentation
7. Filtration

The filter was piped in parallel with a slant-tube clarifier. Flexibility was provided for loading the filter with flocculated wastewater or effluent from the clarifier. During the sampling program, the clarifier was loaded at 60 gpm (1.5 gpm/ft^2) when the filter was not in use. The filter was loaded at 40 gpm (1.5 gpm/ft^2). The filter bed had a cross-sectional area of 26.5 ft^2 with a media depth of 12 inches. Provision of valves to permit bypass of either unit allowed independent field testing of the

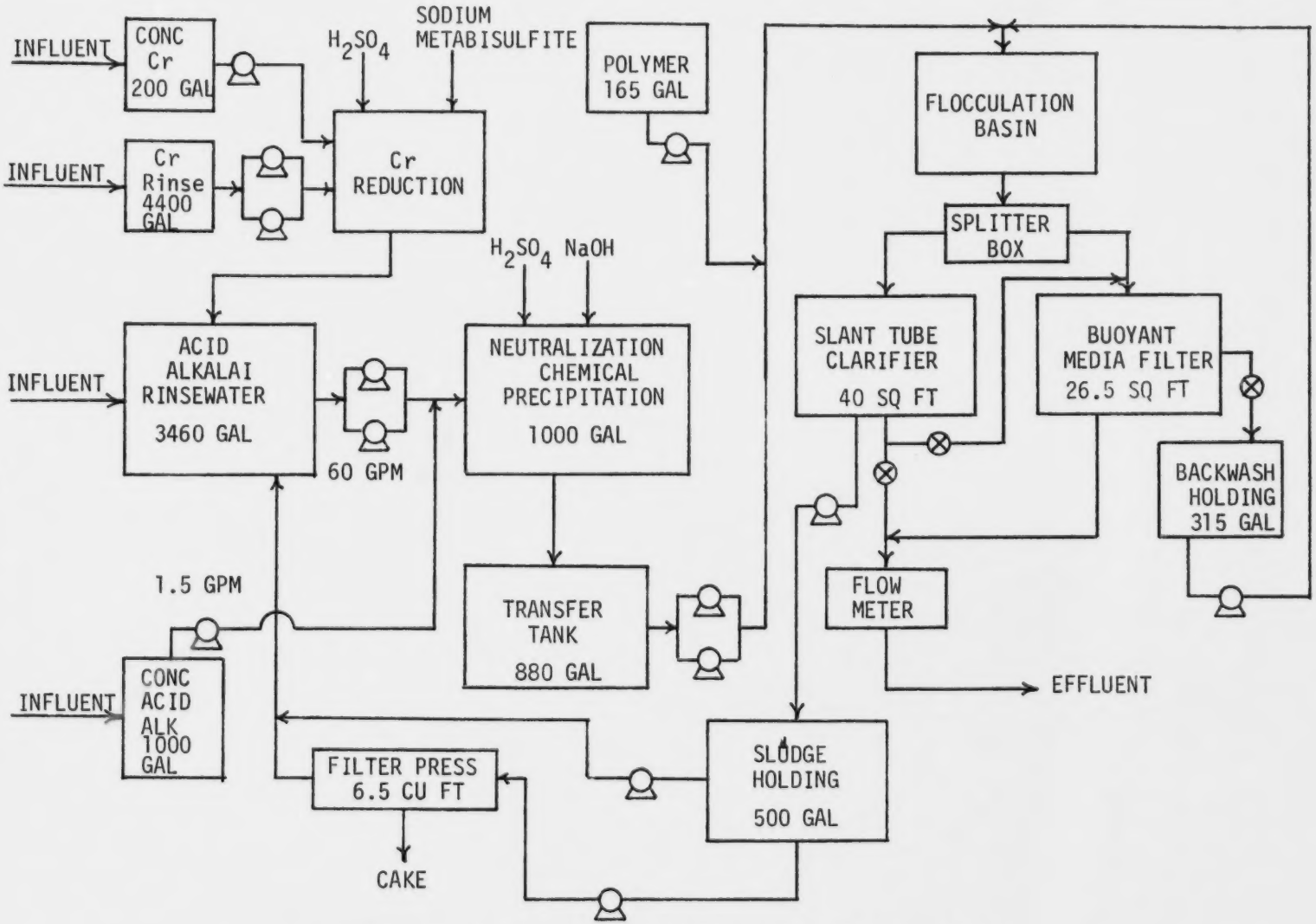

Figure 3. Process flowsheet-buoyant media filtration.

clarifier and filter. A backwash flow rate of 17.4 gpm/ft^2 was employed, representing a total volume of 7.5 gal/ft^2 backwash quantity.

SAMPLING PROGRAM

Objectives

The objectives of the field evaluation program for the buoyant media filter are summarized below:

1. Characterization of steady-state performance of slant-tube clarifier.
2. Characterization of steady-state performance of buoyant media filter without pretreatment by clarification.
3. Characterization of dynamic performance of slant-tube clarifier when subjected to variation in flow rate.
4. Characterization of dynamic performance of buoyant media filter when subjected to variation in flow rate.

Sample Location and Frequency

Steady-State Clarifier Performance--

The performance of the clarifier was evaluated by operation of the treatment system in a mode with by-pass of the buoyant media filter. Operation of the system in this mode for three processing shifts allowed adequate sample collection to fully characterize the system performance. It is noted that this system configuration corresponds with the conventional practice.

A combination of grab and flow-proportional composite samples was obtained to characterize the influent and effluent streams. Individual samples were collected at flow intervals of 2,000 gallons based on the flow totalizer. This interval corresponded with a time interval of approximately thirty minutes at average flow conditions. Equal volume aliquots were composited for the duration of the process shift to obtain a single composite sample. Discrete grab samples were retained for analysis as well.

Steady-State Filter Performance--

The performance of the filter was evaluated by operation of the system in a mode with by-pass of the clarifier. Comparison of the performance data with the conventional system enabled identification of the performance benefits associated with the new filtration technology.

An identical sample collection program was employed as described for characterization of the clarifier performance extending over four operating shifts. In addition, three grab samples of the filter backwash stream were collected.

Dynamic Response of Clarifier--

The hydraulic loading on the wastewater treatment system was subject to periodic fluctuations associated with pumping cycles from the equalization basin. The performance of the clarifier under variable flow conditions was assessed by development of time series response data corresponding with initiation of a pumping cycle. Effluent grab samples were collected at the clarifier discharge at one minute intervals for a total period of fifteen minutes following initiation of a pumping cycle. Characterization of the dynamic response was completed for two independent pumping cycles.

Dynamic Response of Buoyant Media Filter--

An identical sample collection program as described above was pursued to define the dynamic response of the filter when operated without pretreatment by clarification.

Analytical Program

Differentiation between soluble and particulate forms of the metals of interest was beneficial in characterizing the performance of the physical operations involved. Removal of soluble metal forms was not expected during sedimentation or filtration. Due to periodic problems with the chromium reduction system, the clarifier or filter influent was observed to contain

significant concentrations of soluble chromium on several occasions during the sampling program. The influent and effluent composite samples were analyzed for the following parameters:

1. Cr (Total and Dissolved)
2. Zn (Total and Dissolved)
3. Cu (Total and Dissolved)
4. Fe (Total and Dissolved)
5. P (Total and Dissolved)
6. pH
7. TSS

Grab samples were analyzed only for total metals (Cr, Zn, Cu, Fe) and phosphorous.

Analytical procedures are identified in Appendix B.

Results

The steady-state clarifier performance was determined by the composite sampling effort and is summarized in Table 4. Data are reported for influent and effluent samples. It is noted that for the purposes of this study, influent refers to wastewater after chemical precipitation and flocculation. Thus the influent and effluent samples corresponded to sample locations immediately upstream and downstream from the clarifier, respectively.

The filter performance as characterized by the composite sampling efforts is summarized in Table 5. In this context, influent and effluent samples corresponded to sample locations immediately upstream and downstream from the buoyant media filter, respectively.

Based on the composite sample results, both the clarifier and the filter achieved compliance with the effluent limitations reported in Table 1. This performance efficiency was achieved in spite of the elevated concentration of metals and suspended solids in the influent stream. In certain cases, problems were experienced with removal of chromium. This difficulty was attributed to an incomplete reduction of hexavalent chromium to the trivalent form, as evidenced by very high levels of soluble chromium in the effluent. The effluent concentrations and removal efficiencies were

TABLE 4. CLARIFIER PERFORMANCE-COMPOSITE SAMPLES

Parameter	Influent	Effluent	% Removal
April 2, 1984			
Zn, total, mg/L	119.7	0.80	99.3
P, total, mg/L	11.4	0.26	97.7
Cu, total, mg/L	17.4	0.10	99.4
Fe, total, mg/L	37.3	0.06	99.8
Cr, total, mg/L	61.7	11.80(a)	80.9
Suspended solids, mg/L	1052	14.2	98.7
April 5, 1984			
Zn, total, mg/L	108.1	0.91	99.2
P, total, mg/L	50.8	0.44	99.1
Cu, total, mg/L	1.7	0.20	88.2
Fe, total, mg/L	43.0	0.11	99.7
Cr, total, mg/L	16.8	0.05	99.7
Suspended solids, mg/L	790	13.5	98.3

(a) Incomplete reduction of chromium due to malfunction of chemical feed system. Soluble chromium concentration was equal to 11.53 mg/L.

TABLE 5. BUOYANT MEDIA FILTER PERFORMANCE-COMPOSITE SAMPLES

Parameter	Influent	Effluent	% Removal
April 3, 1984			
Zn, total, mg/L	97.9	0.88	99.1
P, total, mg/L	14.3	0.60	95.8
Cu, total, mg/L	6.6	0.72	89.1
Fe, total, mg/L	28.4	0.18	99.4
Cr, total, mg/L	19.6	0.04	99.8
Suspended solids, mg/L	685	40.0	94.2
April 4, 1984 (3rd shift)			
Zn, total, mg/L	109.7	0.63	99.4
P, total. mg/L	60.3	1.31	97.8
Cu, total, mg/L	2.5	0.27	89.2
Fe, total, mg/L	44.0	0.09	99.8
Cr, total, mg/L	24.8	0.05	99.8
Suspended solids, mg/L	838	15.0	98.2
April 4, 1984 (1st shift)			
Zn, total, mg/L	23.0	0.64	97.2
P, total. mg/L	9.7	0.92	90.5
Cu, total, mg/L	2.5	0.93	62.8
Fe, total, mg/L	7.6	0.20	97.4
Cr, total, mg/L	2.2	<0.01	99.5
Suspended solids, mg/L	122	7.0	94.3

comparable for the two systems. A statistical evaluation of the data was not undertaken for the composite samples to determine whether the differences were significant because of the limited number of sample replicates.

The results of the grab sampling effort for influent, clarifier effluent, and filter effluent are summarized in Table 6. These data represent a cumulative statistical analysis for the 71 grab samples which were analyzed for the entire week. Several analyses for total chromium were not incorporated into the statistical summary because temporary problems were encountered with the chromium reduction system. It was believed that evaluation of performance under these conditions would not be representative due to the excessive levels of soluble chromium.

Based on the grab samples, it is apparent that considerable variations in both influent and effluent concentrations were experienced. A statistical evaluation was pursued with the grab sample data to determine whether the reported differences in effluent concentration between the filter and clarifier were significant. Details of the statistical analysis are included in Appendix C.

The clarifier appeared to suffer a more pronounced variation in effluent quality than the filter in view of the greater standard deviation of effluent values. This difference was determined to be significant for Zn, P, Fe, and Cr.

The average and maximum effluent concentrations were also normally greater during operation with the clarifier. This difference was determined to be significant for Zn and Cr.

It should be pointed out that the experimental testing of the clarifier and filter was not conducted with side-by-side experimental units receiving identical wastewater inputs. It is implicit in the preceding analysis that the influent characteristics were comparable for the different time periods corresponding to sequential testing of each unit.

A total of four dynamic tests were completed to characterize the system response to variations in the influent flow rate. In each study, the hydraulic loading was increased in a step forcing from 0 to approximately 1.5 gpm/ft^2. The time series response was monitored for a period of 15 minutes. The results are presented in Table 7. Data are reported for

TABLE 6. STATISTICAL SUMMARY OF GRAB SAMPLE DATA

Parameter	Clarifier Influent	Clarifier Effluent	Clarifier % Removal	Filter Influent	Filter Effluent	Filter % Removal
Zn, total						
Mean, mg/L	82.8	1.69	98.0	71.0	0.79	98.9
Standard deviation, mg/L	44.2	1.37		48.2	0.32	
Maximum, mg/L	142.6	5.92		129.3	1.34	
Minimum, mg/L	3.1	0.67		3.2	0.36	
Number of Data Points	13	13		23	22	
P, total						
Mean, mg/L	36.7	2.12	94.2	29.9	0.87	97.1
Standard deviation, mg/L	30.4	2.71		34.2	1.04	
Maximum, mg/L	98.1	9.97		156.5	5.13	
Minimum, mg/L	3.7	0.19		1.7	0.09	
Number of Data Points	13	13		23	22	
Cu, total						
Mean, mg/L	13.1	0.51	96.1	5.8	0.55	90.5
Standard deviation, mg/L	3.6	0.62		7.8	0.42	
Maximum, mg/L	86.1	1.93		34.6	1.38	
Minimum, mg/L	0.2	0.11		0.4	0.13	
Number of Data Points	13	13		23	22	
Fe, total						
Mean, mg/L	32.5	0.27	99.2	29.8	0.13	99.6
Standard deviation, mg/L	20.2	0.34		27.4	0.11	
Maximum, mg/L	69.0	1.31		90.6	0.51	
Minimum, mg/L	< 0.1	0.03		0.8	0.02	
Number of Data Points	13	13		23	22	
Cr, total						
Mean, mg/L	17.6	0.20	98.9	15.9	0.03	99.8
Standard deviation, mg/L	20.1	0.25		17.4	0.04	
Maximum, mg/L	64.7	0.76		54.0	0.18	
Minimum, mg/L	< 0.1	<0.01		0.2	<0.01	
Number of Data Points	9	9		21	20	

TABLE 7. DYNAMIC RESPONSE SUMMARY

Time (Min)	Effluent Zinc Concentration (mg/L)			
	Clarifier		Filter	
	Run 1(a)	Run 2(b)	Run 1(c)	Run 2(d)
1	0.82	0.75	0.88	0.55
2	0.70	0.81	0.87	0.48
3			0.88	0.47
4	1.51	0.77	0.88	0.43
5	1.63	0.79	0.85	0.44
6	1.19	0.82	0.83	0.49
7	1.03	0.81	0.84	0.44
8	1.40		0.87	0.44
9	1.20	0.83	0.85	0.50
10	1.20	0.84	0.81	0.44
11	1.03	0.78	0.77	0.50
12	1.23	0.90	0.77	0.42
13	1.11	0.94	0.75	0.42
14	0.97	0.90	0.82	0.45
15	0.85	0.86	0.82	0.43
16	0.77			

(a) Influent zinc concentration equal to 104 mg/L.

(b) Influent zinc concentration equal to 88 mg/L.

(c) Influent zinc concentration equal to 27 mg/L.

(d) Influent zinc concentration equal to 112 mg/L.

total zinc concentration in the system effluent as an indicator of removal of all particulate species.

Neither the clarifier or the filter exhibited an unacceptable response to changes in hydraulic loading. Clarifier performance was affected slightly by the flow increase in Run #1, although a similar effect was not evident in the second clarifier dynamics test. The filter did not evidence any systematic response to the change in flow.

EVALUATION OF PROCESS

Energy Requirements

The energy requirements for operation of the buoyant media filter were minimal. The system operated with a head loss of a few inches. Backwash of the filter was achieved via gravity flow, so that the power consumption associated with backwash operations in a standard configuration filter was avoided. Backwash volume requirements represented approximately six percent of product water during the evaluation period.

Cost

A preliminary estimate of capital costs (1984 cost basis) for the buoyant media filter systems was provided by 3M, as summarized in Table 8. The quoted prices include the filter structure, filter media, filter inlet and outlet connections, and electrically operated backwash valve. The price does not include a control system for backwash or a control panel. The price of the media alone is approximately $70/cubic foot.

Estimation of operating costs for the buoyant media filter cannot be completed with reliability due to the absence of data for any sustained period of operation. The system has been operated sporadically to demonstrate the process, thus cost data for a sustained period does not exist. Based on available information at this time, costs for replacement of filter media do not appear to be significant. Automation of the backwash cycle appears to be generally feasible, so that labor requirements would be minimal. Maintenance costs would also be expected to be minimal due to the

TABLE 8. BUOYANT MEDIA FILTER CAPITAL COST ESTIMATE

Hydraulic Capacity	Capital Cost (not installed)
12 gpm	$10,400
24 gpm	15,600
36 gpm	21,400
48 gpm	26,600
72 gpm	38,000

absence of pumps. It is noted that one valve is present in the system which may require limited maintenance.

Safety Considerations

The buoyant media filtration system did not present any adverse safety considerations in comparison with a conventional treatment process.

Required Operator Skill

Operation of the buoyant media filter did not appear to require special operator skills. In fact, automation of the backwash cycle would be expected to minimize required decisions and operator attention to the system. An extensive operating history was not available to evaluate troubleshooting requirements or to anticipate potential operating problems which may require an innovative operator response, such as incomplete removal of precipitated solids from the media surface.

Degree of Applicability

Application of the buoyant media filtration concept to upgrade existing conventional precipitation and clarification systems would seem to be generally feasible. Installation of a retaining screen, filter media, and backwash withdrawal system on a conventional clarifier would be possible as

long as adequate head space was available. Head loss requirements are not of sufficient magnitude to preclude application in most cases. The buoyant media filtration process may also be compatible with additional solids-liquid separation processes besides chemical precipitation of metal-bearing wastewaters. Investigations involving secondary clarification of municipal wastewaters have also been initiated by 3M.

Advantages and Limitations of Process

The buoyant media filter unit in operation at the 3M facility was demonstrated to be a viable alternative to the existing slant-tube clarifier. Both systems were capable of removal of particulate metal hydroxide precipitates to required effluent standards for this application. It is noted that negligible removal of soluble materials was experienced, so that compliance would be sensitive to the success of preceding chemical reduction and precipitation processes. The characteristics of the buoyant media filter were similar in this respect to the conventional system.

Analysis of numerous grab samples over the extended sampling period indicated an enhanced stability of performance of the filter in comparison to the slant-tube clarifier. This observation is significant, in view of the highly variable nature of the influent wastewaters at this particular metal finishing operation. Numerous batch dumps of cleaning or plating solutions were experienced throughout an operating day. Radical variation in influent wastewater characteristics was noted, with extreme variation in solids and hydraulic loading on the two solids-liquid separation systems. The demonstrated stability of the filter under these conditions is an important advantage.

Removal of soluble metal species was not expected during a physical operation such as gravitational sedimentation or filtration. This limitation of the process was documented. Addition of buoyant media filtration to an existing system would not appreciably improve performance in those instances where the principal metal species remaining after chemical precipitation was not in a particulate form.

SECTION 6

ZERPOL ZERO LIQUID DISCHARGE

PROCESS DESCRIPTION

The Zerpol® process achieves zero discharge of liquid effluent via a strategy for recycle and reuse of treated effluents as rinsewater. Production of a high purity rinsewater is practiced by condensation of steam generated by a boiler receiving treated rinsewaters as feed. Residual salts and solids are removed from the system as boiler blowdown and metal hydroxide sludge, respectively. These streams are removed by contract hauling and disposal. The Zerpol® process is protected by U.S. Patent 4,437,968. Additional applications are pending.

Chemical treatment of the rinsewaters is conducted in a batch mode, with sequential treatment in a single reactor for cyanide oxidation, chromium reduction, metal hydroxide precipitation, and sedimentation. Certain restrictions are imposed on selection of the reagents employed for the chemical treatment operations in order to reduce the input of dissolved species to the recovery loop of the system. Hydrogen peroxide is used for oxidation of cyanide in lieu of the conventional chlorine compounds which would result in unacceptable levels of chloride in the system. Sodium hydrosulfite is used for chromium reduction because a pH near neutral is effective (pH = 5 to 8). This neutral pH eliminates the requirement for addition of large quantities of salts for reduction of pH to optimum levels for reaction with bisulfite salts or sulfur dioxide. Precipitation of the metal species is achieved by addition of sodium hydroxide. Sodium salts are favored over calcium salts to avoid scaling problems in the boiler.

System Configuration

The Zerpol® treatment system is characterized by large tank volumes to accommodate the batch treatment mode of operation. A simplified schematic diagram of the process is provided as Figure 4. All influent wastewaters are collected in one of the two batch reaction tanks. A treatment cycle is initiated when the capacity of one of the tanks is exhausted. The tanks are designed to hold the entire wastewater flow for a duration of 3 days. Influent wastewaters are diverted to the alternate batch treatment tank during a batch treatment cycle. Oils are skimmed from the surface and collected in a chamber located between the two batch treatment tanks.

After chemical treatment for cyanide oxidation, chromium reduction, and hydroxide precipitation, the precipitated solids are allowed to settle overnight in the batch reactor. Settling aids are not normally used. Supernatant is withdrawn and retained as make-up water for rinsing operations. This supernatant is stored in the clear water storage tank.

The precipitated solids are removed from the batch reactor and transferred to a gravity thickener. The thickener has sufficient capacity to permit withdrawal and disposal of sludge on an infrequent basis. The facilities which were surveyed disposed of sludge from the thickeners at intervals of two to six months.

A portion of the effluent (approximately one third of the flow) from the batch treatment process is directed to a boiler for production of steam. The remaining batch effluent (two thirds of flow) is used directly as rinsewater. The steam is used for various process applications throughout the plant, including heating plating solutions, heating hot water rinses, and evaporation of water from collected boiler blowdown.

The input concentration of dissolved salts to the boiler is extremely high (several thousand mg/L). This level of salts in a boiler feed would be of general concern, if precautions and safeguards were not practiced to control the chemical composition of the boiler feed stream. Specifically, a small concentration (several mg/L) of residual cyanide is purposely left in the effluent from the batch treatment process. This residual cyanide acts as an oxygen scavenger, inhibiting corrosion of boiler surfaces. Additional chemicals (e.g., chromium) may be added to the boiler feed as necessary to

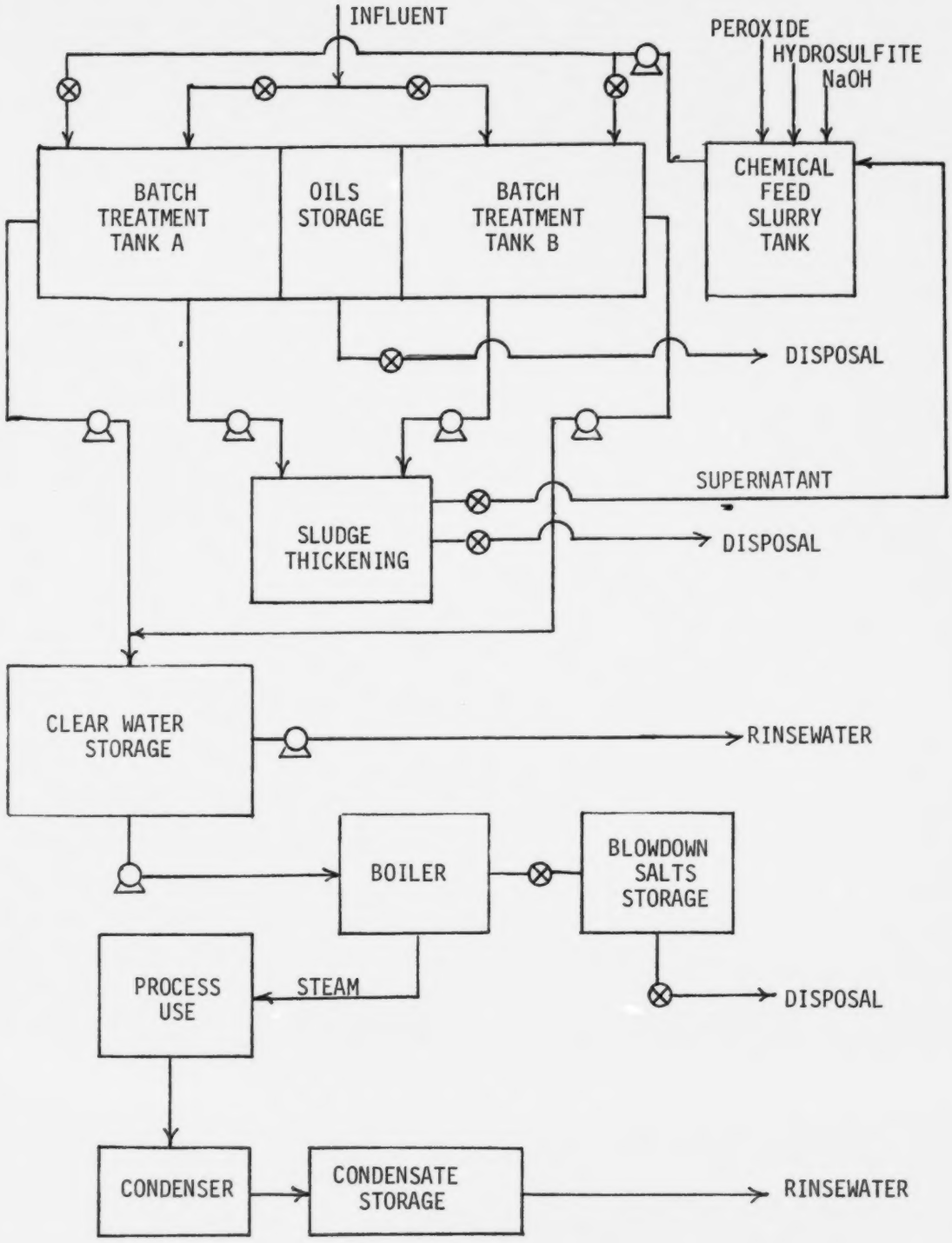

Figure 4. Zerpol zero liquid discharge schematic.

prevent scaling and assure proper boiler function. Nominal quantities of chromium (several mg/L) may be desired as a residual after batch treatment for this reason.

Salts are removed from the system periodically as boiler blowdown. Thickening and evaporation of the blowdown stream is achieved in a separate tank. Salts are removed from this tank on an infrequent basis (several times per year).

A source of make-up water is required to compensate for the material which evaporates from the plating solutions and cleaners which are removed from the process via disposal of sludge and salts. The presence of small amounts of calcium or magnesium in the raw water source may result in accumulation of these ions to objectionable levels from the standpoint of operation of the boiler. Consequently, provision of a water softening system is essential to maintain proper boiler function if the source water is not soft.

Due to the extended hydraulic detention in the treatment system components, successful water conservation and flow reduction are essential factors for attainment of a zero liquid discharge condition.

Zerpol® Applications Surveyed in this Program

Pioneer Metal Finishing - Franklinville, NJ --

Pioneer Metal Finishing is a job shop operation dealing primarily in decorative plating of copper, nickel, and chromium. Base materials include zinc, brass, steel and cast iron. The major production effort during the sampling effort consisted of rack plating of well-drained pieces, so that dragout was a minimum.

The configuration of the plating lines is presented in Table 9. Information regarding plating bath chemistry is noted in Table 10. Installation of the counterflow rinsing system was completed concurrently with construction of the Zerpol® treatment system. Implementation of the water conservation program was effective in reducing flows from 30,000 to 5,000 gallons per shift. A two-shift operation was experienced during the sampling effort.

TABLE 9. PLATING LINE CONFIGURATION

PIONEER METAL FINISHING

Tank	Volume (Gallons)
Die Cast Soak	1700
Steel Soak	1700
Overflow Rinse	700
Diecast Electrolytic Cleaner	1000
Steel Electrolytic Cleaner	1000
Counterflow Rinse	700
Counterflow Rinse	700
Sulfuric Acid (2%)	1000
Muriatic Acid	1000
Counterflow Rinse	700
Counterflow Rinse	700
Copper Strike (CN)	1000
Copper Bright (CN)	1000
Copper Bright (CN)	2400
Counterflow Rinse	700
Counterflow Rinse	700
Sulfuric Acid (0.5%)	700
Duplex Nickel	700
Nickel	1000
Nickel	1700
Nickel	1700
Nickel	1500
Counterflow Rinse	700
Counterflow Rinse	700
Counterflow Rinse	700
Trivalent Chrome	1000
Trivalent Chrome	1000
Counterflow Rinse	700
Counterflow Rinse	700
Counterflow Rinse	700
Hot Rinse (Condensate Input)	700

TABLE 10. PLATING BATH SOLUTIONS
PIONEER METAL FINISHING

Solution	Chemical
Diecast Soak	Fred Gumm Ionic Soak
Steel Soak	Fred Gumm Ionic Soak
Diecast Cleaner	Fred Gumm 502 B
Steel Cleaner	Cleanite 77
Copper Bright	M & T Copperlume
Duplex Nickel	M & T Permolume G
Nickel	M & T Superlume II
Trivalent Chrome	Harshaw Tri Chrome
Trivalent Chrome	Envirochrome

The Zerpol® system has been in operation at Pioneer Metal Finishing since 1981. A process flowsheet for the waste management system is detailed in Figure 5. Tank capacities are also indicated. It should be noted that there was no condensate storage tank in this system. Condensate was routed directly for use as make-up in the hot water rinse system. In the event of a boiler malfunction with a resulting contamination of condensate with salts, the condensate was returned to the clear water storage tank.

Selected photographs of this Zerpol® installation are included in Appendix D.

Plate-Rite Co. - Folcroft, PA--

Plate-Rite Co. operates a job shop for a variety of metal finishing and plating operations and non-destructive testing. A partial list of operations is noted below:

1. Cadmium: Barrel and Rack. Bright, yellow, olive drab and phosphate conversion coatings.
2. Zinc: Barrel and Rack. Same supplementary coatings as cadmium.
3. Copper: Barrel and Rack. Non-decorative.
4. Silver: Barrel and Rack. Non-decorative, Matte Finish.
5. Passivation: Stainless and corrosion resistant steels.
6. Phosphates: Zinc and manganese phosphate.

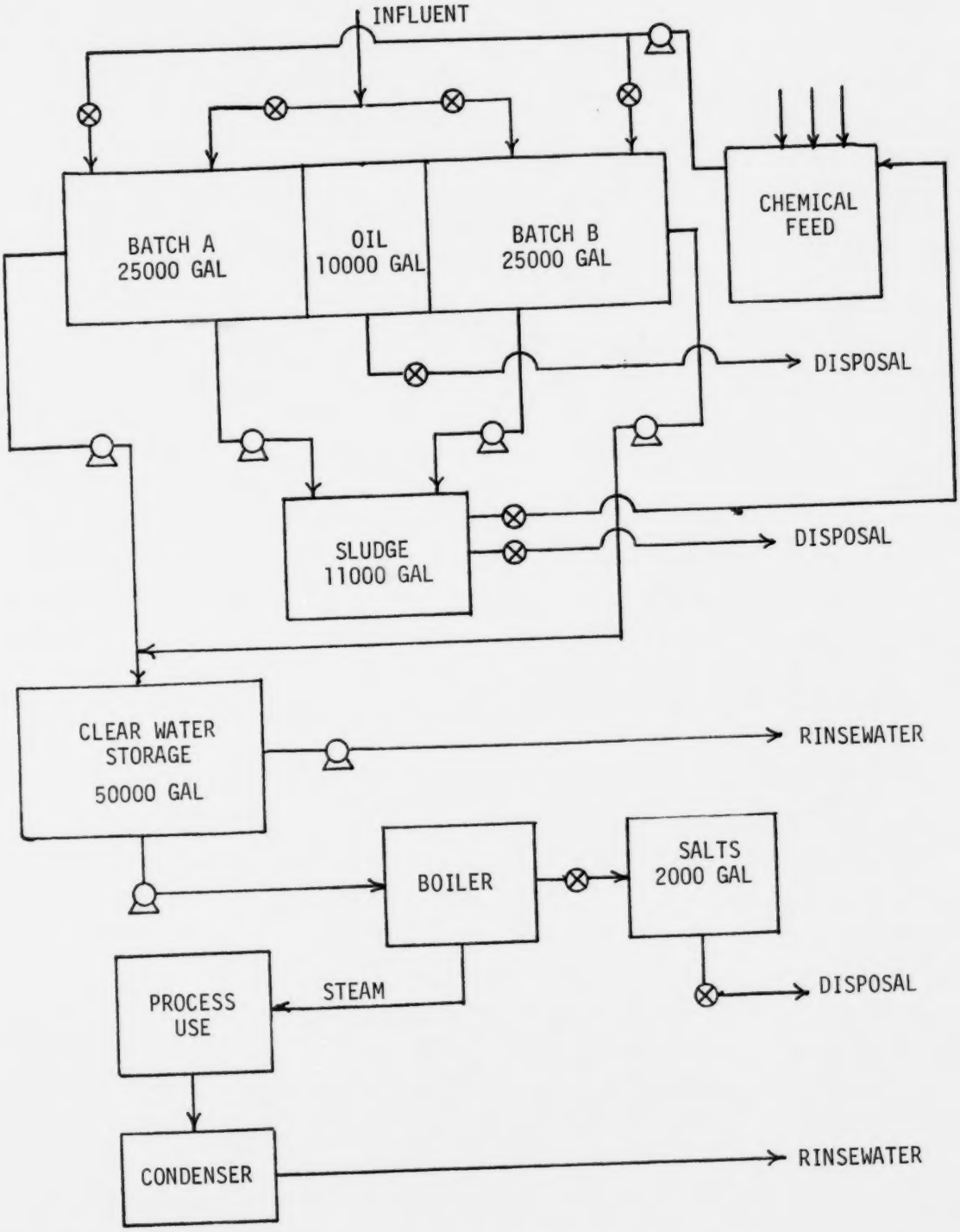

Figure 5. Process flowsheet-Pioneer Metal Finishing.

7. Black Oxide: Various specifications for steel, stainless, copper and brass.
8. Chem Film Coating for Aluminum.

A partial characterization of the plating line configuration is provided in Table 11. This description is limited to the dominant processes which were in use during the sampling period. A description of the plating solutions is provided in Table 12. The wastewater flow was approximately 2500 gallons per day. A process flowsheet for the Plate-Rite Co. treatment system is presented in Figure 6, including tank volumes.

James Spring and Wire Company - Frazer, PA--

Barrel plating of zinc and cadmium are conducted on various springs (steel, nickel, and copper alloy) in this small captive plating operation. The wastewater contains large quantities of oils in comparison to the other two facilities which were surveyed.

The plating lines include alkaline cleaners, acid treatment, CN plating baths, zinc phosphating, chromate rinse, and counterflow rinsing. Analysis of the plating bath solutions is reported in Table 13.

The James Spring and Wire treatment system was the original Zerpol® system; it has been operational for a period of five years. The system configuration is noted in Figure 7 with tank volumes as indicated. A slight modification of the process to incorporate rainwater collection and storage was undertaken to supplement the supply of condensate. This approach allowed suspension of operation of the boiler during much of the hot weather period. Acceptable product quality was maintained when treated effluent was used exclusively for rinsewater make-up without supplementation by condensate derived from operation of the boiler. The estimated daily wastewater flow for this facility was 4500 gallons.

TABLE 11. PLATING LINE CHARACTERIZATION
PLATE-RITE CO.

BARREL PLATING - Zn, Cd

Soak Cleaner
Overflow Rinse
Electrocleaner
Counterflow Rinse
Counterflow Rinse
Hydrochloric Acid Pickle
Counterflow Rinse
Counterflow Rinse
Counterflow Rinse
Low CN Zinc Plating Bath
Low CN Zinc Plating Bath
Low CN Zinc Plating Bath
Cadmium Plating Bath
Cadmium Plating Bath

BARREL PLATING - Cu

Copper Plating Bath
Counterflow Rinse
Counterflow Rinse
Counterflow Rinse
Nickel Strike
Yellow Chromate
Counterflow Rinse
Counterflow Rinse
Chromate Bright (Cd)
Counterflow Rinse
Chromate Bright (Zn)
Counterflow Rinse
Hot Rinse (Condensate Input)

RACK OPERATIONS

Alkaline Soak Cleaner
Rinse
Non-Chromate Deoxidizer
Rinse
Aluminum Conversion Coating
Rinse
High CN Zinc Plating
Counterflow Rinse
Counterflow Rinse
Counterflow Rinse

TABLE 12. PLATING BATH SOLUTIONS

PLATE-RITE COMPANY

Process	Component	Concentration (Oz./Gallon)
Zn - Barrel	Zn	2 to 3
	CN	3 to 6
	NaOH	9 to 15
	Carbonates	< 8
	Brightener	
Cd - Barrel	Cd	2.7 to 3.5
	CN	15 to 18
	NaOH	1 to 3
	Carbonates	< 8
	Brightener	
Cu - Barrel	Cu	3 to 4
	CN	0.5 to 2.0
	Rochelle Salts	6
	Optimum pH	9.6
Nickel Strike	Nickel Chloride	20
	HCl	10
Zn - Rack	Zn	3 to 6
	CN	8 to 20
	NaOH	10 to 15
Cd - Rack	Cd	2.7 to 3.5
	CN	15 to 18
	NaOH	1 to 3
Silver	Ag	3 to 3.25
	KCN	5 to 7.5

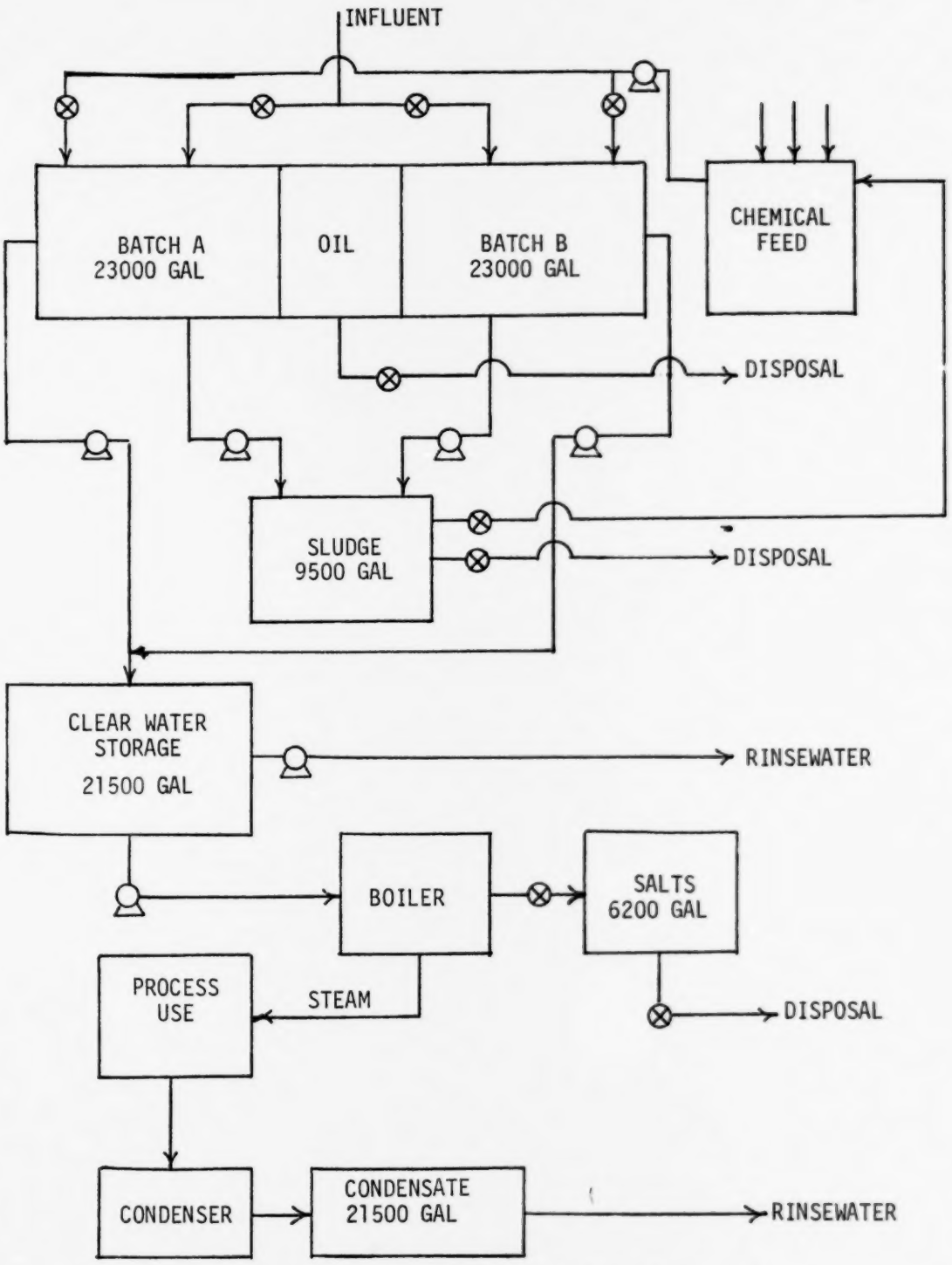

Figure 6. Process flowsheet-Plate-Rite Company.

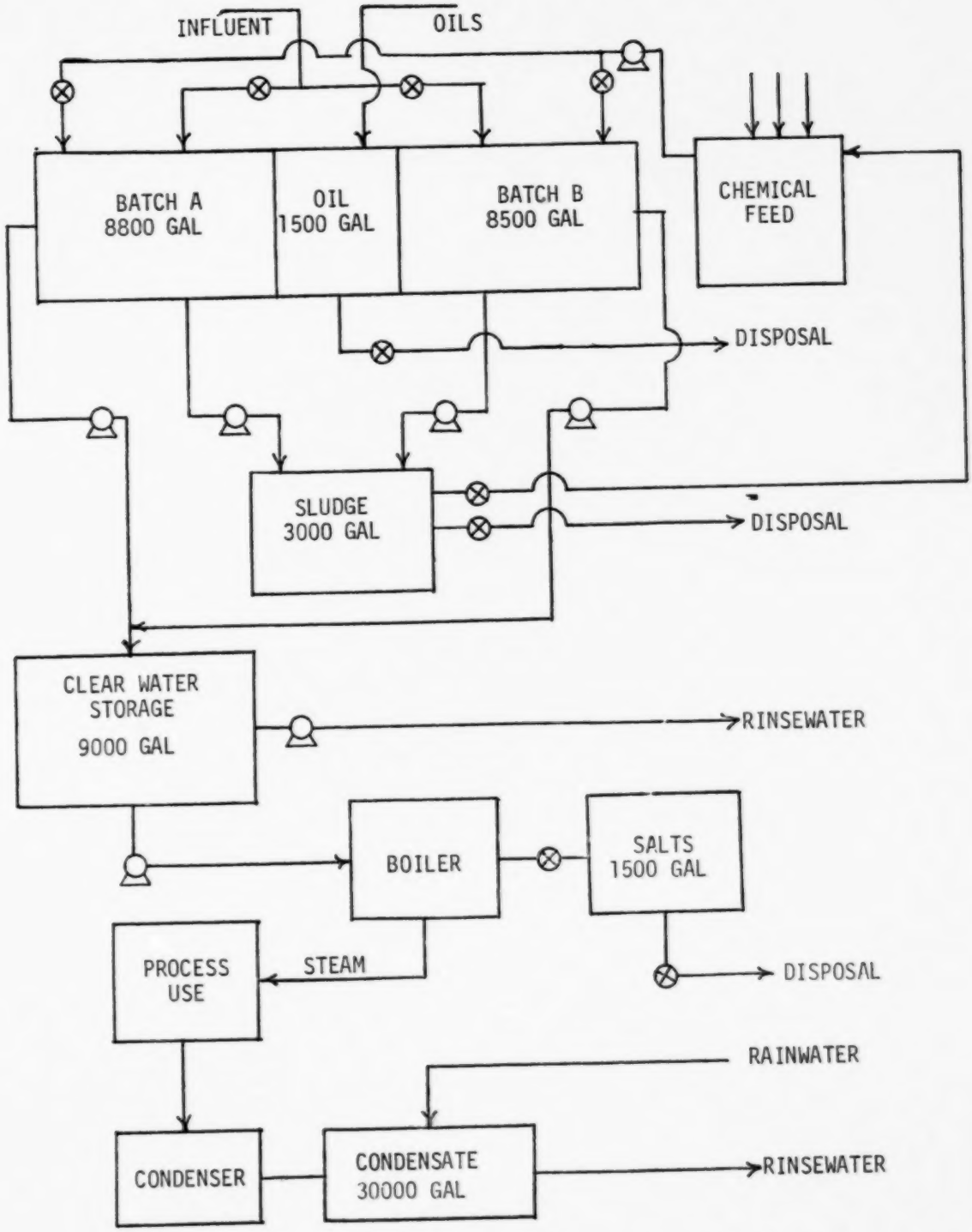

Figure 7. Process flowsheet-James Spring and Wire Company.

TABLE 13. PLATING BATH SOLUTIONS
JAMES SPRING AND WIRE COMPANY

Process	Component	Concentration (Oz./Gallon)
Zn - Barrel	Zn	3.6
	NaCN	9.2
	NaOH	9.6
Cadmium Barrel	Cd	1.4
	NaCN	12.6
	NaOH	2.4
Oil - Rust Prevention	Parcoloc 2945	

SAMPLING PROGRAM

Objectives

A complete definition of a material balance on a Zerpol® process would require an extended sampling presence due to the extended detention of sludge in the gravity thickener. This sampling effort was limited to examination of one batch treatment cycle at each of the three facilities to develop preliminary data for description of system performance. Specific objectives are noted below:

1. Identification of time averaged raw wastewater characteristics over a time period corresponding to a single batch cycle. These composite samples were obtained from the batch treatment tanks immediately prior to initiation of a treatment cycle.
2. Identification of time averaged batch treated effluent characteristics corresponding to the same batch cycle as the influent characterization.
3. Characterization of condensate stream. Due to the absence of separate condensate storage facilities at Pioneer Metal Finishing, condensate samples could only be collected as discrete grab samples. The configuration at James Spring and Wire was not conducive to isolation of condensate since rainwater was also added

to the stored condensate. The condensate storage at Plate- Rite had been contaminated with treated effluent prior to the sampling period, so that collection of a composite sample from that tank would not be representative of the condensate stream. For the reasons cited above, all condensate samples were collected at one point in time as discrete grab samples. A series of grab samples was obtained at Pioneer Metal Finishing to assess variability.

4. Characterization of boiler blowdown. These samples were collected as grab samples during the sampling period. Withdrawal of samples from the salts storage tank was not believed to afford representative samples due to evaporative losses.
5. Characterization of sludge. The compositing period for the sludge samples did not correspond to the single batch cycle.
6. Characterization of influent variability. A series of grab samples were obtained of the total influent flow at Pioneer Metal Finishing.

Sample Location and Frequency

Grab samples were collected from each of the following sampling stations for each facility:

1. Influent storage
2. Batch treatment effluent
3. Condensate
4. Boiler blowdown
5. Chemical precipitate sludge

The composition of these grab samples reflected average conditions through the time period corresponding to a single batch cycle, with the exception of condensate as previously noted. Compositing of discrete samples over an extended period was therefore not required to obtain a sample representative of the batch cycle. Three replicate samples were obtained for each sampling station.

Ten additional grab samples were collected of the influent and condensate at Pioneer Metal Finishing at different times in one operating day to assess short-term variability.

Analytical Program

Composite samples were analyzed for each of the five sampling locations for the following parameters: Ca, Cd, Cr, Cu, Fe, Mg, Ni, Zn, CN, P, pH, TSS, and TDS.

The discrete grab samples for the Pioneer Metal Finishing influent were analyzed for the same parameters except TSS and TDS. The Pioneer Metal Finishing grab condensate samples were analyzed for total solids. Studies were not completed to determine the leaching characteristics of the generated sludges.

Results

The results of the analysis for the composite samples are presented for each industry in Tables 14-16. The results of the grab samples from Pioneer Metal Finishing are presented in Tables 17-18. The data are reviewed individually for each facility.

The sampling results for Pioneer Metal Finishing indicated an abnormally high concentration of copper and cyanide. A small leak in a heating coil in one of the copper plating baths was discovered after conclusion of the sample collection effort. This anomaly produced non-representative levels of copper, cyanide, and TDS throughout the system (i.e., influent, effluent, condensate, and boiler blowdown). The cyanide concentrations in particular exceeded target values for both treated effluent and condensate.

The residual metals concentrations after batch treatment did not approach values which would be permissible for discharge. The quality of the condensate would also preclude discharge due to the cyanide and copper contamination. Because these streams are recycled for rinsing purposes, the critical concerns relate to maintenance of an acceptable product quality rather than compliance with an environmental standard. Satisfactory product quality was maintained throughout the "upset" associated with the heating coil leak.

The performance data from Plate-Rite closely resembled desired operating conditions. The reported value for influent cyanide was somewhat greater than normally experienced at Plate-Rite, but the treated effluent

TABLE 14. ZERPOL ZERO LIQUID DISCHARGE
PIONEER METAL FINISHING - COMPOSITE SAMPLES

Parameter	Influent	Treated Effluent	Condensate	Sludge	Boiler Blowdown
Ca, mg/L	2.8	2.4	0.16	92	0.34
Cd, mg/L	0.01	< 0.01	< 0.01	1.2	< 0.01
Cr, mg/L	37	0.83	< 0.01	2840	20
Cu, mg/L	210	100	47	1590	73
Fe, mg/L	24	0.47	3.8	4070	1.5
Mg, mg/L	1.1	1.1	0.02	36	< 0.01
Ni, mg/L	200	79	1.3	6640	210
Zn, mg/L	8.1	0.55	0.72	1390	< 0.01
CN, mg/L	1140	220	20	530	58
P, mg/L	7.8	1.7	0.68	380	< 0.01
TSS, mg/L	990	130	2.6	48,200	1750
TDS, mg/L	9940	9550	700		293,000
pH	8.4	9.1	9.5	7.1	9.9

TABLE 15. ZERPOL ZERO LIQUID DISCHARGE
PLATE-RITE COMPANY - COMPOSITE SAMPLES

Parameter	Influent	Treated Effluent	Condensate	Sludge	Boiler Blowdown
Ca, mg/L	12	8.1	3.3	350	9.6
Cd, mg/L	46	13	2.7	1150	18
Cr, mg/L	170	1.2	1.7	3740	14
Cu, mg/L	57	18	2.8	1300	22
Fe, mg/L	42	0.2	0.13	2540	0.86
Mg, mg/L	4.2	5.4	1.3	84	3.6
Ni, mg/L	17	3.2	0.79	1150	5.1
Zn, mg/L	98	13	3.2	2290	24
CN, mg/L	660	3.2	0.5	1230	2.8
P, mg/L	18	1.4	0.22	880	1.3
TSS, mg/L	680	21	14	65,100	180
TDS, mg/L	15600	16200	11800		18600
pH	10.2	8.2	9.1	9.3	9.2

TABLE 16. ZERPOL ZERO LIQUID DISCHARGE
JAMES SPRING AND WIRE COMPANY - COMPOSITE SAMPLES

Parameter	Influent	Treated Effluent	Condensate	Sludge	Boiler Blowdown
Ca, mg/L	9.6	9.1	0.13	350	11
Cd, mg/L	14	17	0.16	350	21
Cr, mg/L	47	73	0.34	790	100
Cu, mg/L	5.8	5.8	1.3	24	13
Fe, mg/L	10	24	0.14	550	21
Mg, mg/L	3.1	3.2	0.07	52	4.5
Ni, mg/L	6.8	5.6	0.02	14	9.3
Zn, mg/L	15	15	0.17	290	22
CN, mg/L	25	11	0.3	69	18
P, mg/L	58	58	0.44	390	97
TSS, mg/L	170	320	3.2	8230	200
TDS, mg/L	9040	9830	85		25,000
pH	8.3	6.8	9.2	9.0	10.7

TABLE 17. ZERPOL ZERO LIQUID DISCHARGE
PIONEER METAL FINISHING - INFLUENT GRAB SAMPLES

Parameter	Mean	Standard Deviation	Maximum	Minimum	Number of Observations
Ca, mg/L	3.4	0.4	4.0	2.7	10
Cd, mg/L	< 0.01	< 0.01	< 0.01	< 0.01	10
Cr, mg/L	8.6	7.8	22.2	1.6	10
Cu, mg/L	140	90	270	40	
Fe, mg/L	20	12	46	7	10
Mg, mg/L	1.3	0.2	1.6	1.2	10
Ni, mg/L	140	70	280	70	10
Zn, mg/L	6.0	2.3	11.0	3.7	10
CN, mg/L	290	80	410	220	5
P, mg/L	2.1	1.1	4.4	0.8	10
pH	7.3	1.6	9.4	4.0	10

TABLE 18. ZERPOL ZERO LIQUID DISCHARGE
PIONEER METAL FINISHING - CONDENSATE GRAB SAMPLES

Condensate	Total Solids
Mean, mg/L	1570
Standard Deviation, mg/L	950
Maximum, mg/L	2340
Minimum, mg/L	4
Number of Observations	10

and condensate cyanide levels were consistent with objectives to minimize corrosion effects. It is apparent from examination of dissolved solids data that the boiler performance was not optimal at the time of collection of condensate grab samples. Considerably smaller values for TDS would be anticipated during ideal boiler operation. It cannot be determined based on these data whether the reported data were representative of boiler performance or indicative of a temporary upset with an associated loss of solids in the steam output.

Due to the presence of high residual metal concentrations, the treated effluent and condensate quality would not be compatible with discharge options. As previously noted, the appropriate concern is related to possible effects on product quality. Satisfactory product quality was maintained during the sampling program with these corresponding characteristics for rinsewater make-up sources.

The results for James Spring and Wire indicate a more dilute raw wastewater, reflecting a relatively greater water use than the other facilities. Drag out was relatively low also, due to the ease of drainage of the pieces in the barrel lines. It was immediately apparent from the data that little removal of metals was achieved during batch treatment. A definitive explanation for this observation was not available, although a solids-liquid separation problem was suspected. An elevated suspended solids concentration was also reported, supporting this theory. The possibility of nonrepresentative sampling cannot be eliminated.

The reported data for cyanide were consistent with the objective to retain a residual throughout the steam loop to minimize corrosion. The

condensate quality (as indexed by TDS) was much better at James Spring and Wire than the other systems. The treated effluent quality was not compatible with discharge. Satisfactory product quality was reported during the sampling period while using rinsewaters with the reported characteristics.

DISCUSSION OF OPERATING EXPERIENCE

Based on conversations with representatives from the three facilities, certain operational practices may cause problems with the Zerpol® process. The principal difficulties were related to operation of the boiler. A brief discussion of these operational difficulties is provided below.

The conventional method for oxidation of cyanide employs alkaline chlorination, with an associated production of chloride ion. Chlorine is normally selected in favor of peroxide owing to a much smaller chemical cost; but in this process, peroxide is used in conjunction with the boiler. Residual cyanide in the boiler feed is destroyed by reaction with dissolved oxygen at the elevated boiler temperature. Use of chlorine is not compatible with the Zerpol® process due to problems with salts accumulation in the rinsewaters and corrosion. Recirculation of treated effluent as rinsewaters with a TDS in excess of 30,000 mg/L was observed to produce spotting problems and unacceptable product quality.

Certain chemicals in cleaning solutions may produce excessive foaming in the boiler. Problems were suspected with borax, silicates, soaps, and gluconates. Substitution of alternate cleaners or addition of boiler feed chemicals was required to achieve satisfactory boiler performance.

Removal of hardness from make-up water sources was necessary to prevent scale deposition in the boiler. Volumetric make-up requirements were quite low, so that adequate make-up water quantities can be supplied with a residential-type water softener or rainwater accumulation.

The general operating experience at these facilities was favorable, although it was reported that a period of several months indoctrination was necessary to work out site-specific problems. It should be noted that these three facilities have all operated successfully in a zero liquid discharge mode for a period in excess of three years.

EVALUATION OF PROCESS

Energy Requirements

Operation of the boiler represented a considerable potential energy demand. It was difficult to generalize with respect to the additional energy consumption associated with production of steam from one-third of the process flow due to a diversity in steam requirements for various process and non-process functions. At James Spring and Wire, it was determined that steam generation in the summer months could not be justified based on heating requirements. In this case, an alternative source of high purity rinsewater (i.e., rainwater) was obtained for use during hot weather periods. The other facilities indicated an increase in energy consumption of 5 to 15 percent associated with operation of the Zerpol® process. This figure would obviously vary considerably depending on specific local factors.

Cost

An analysis of costs is presented based on operating data provided by the three facilities in Table 19. Due to the very small flowrates represented by the facilities, caution is advised in extrapolation of unit costs to larger installations. It is noted that these cost estimates do not include energy consumption associated with operation of the boiler.

The greatest disparity in costs between the systems was associated with chemical purchases. The much greater cost at Plate-Rite Co. was a function of the large quantities of hydrogen peroxide consumed for oxidation of cyanide. The elevated cyanide levels resulted from drag out in the barrel plating lines from irregularly-shaped pieces which did not drain well.

For flows of this magnitude (less than 25,000 gallons per day), batch treatment systems were reported in an EPA development document to be superior to continuous systems based on total annual cost (4). On the basis of these data, the costs for the Zerpol® system may be regarded as comparable to a conventional batch system for small wastewater volumes.

TABLE 19. ZERPOL ZERO LIQUID DISCHARGE
ANNUAL COST SUMMARY

	Pioneer Metal Finishing	Plate-Rite Company	James Spring and Wire Company
Chemicals, $/yr	4,200	22,478	2,903
Labor (@ $10/hr), $/yr	1,040	2,080	1,560
Monitoring, $/yr	300	95	400
Sludge and salts hauling and disposal, $/yr	3,360	8,112	3,950
Repair, Maintenance, $/yr	----	2,853	-----
Total Operating Cost, $/yr	8,900	35,618	8,813
Capital Cost	150,000	140,000	60,000
Flow, gal/day	5,000	2,500	4,500
Operation, days/year	245	260	260
Start Up Date	1981	1981	1980
Original Flow, Gallons/Shift	30,000	40,000	40,000

Safety Considerations

There are several factors to be considered with regard to safety of the Zerpol® process. In comparison to a conventional system, the Zerpol® process generates a similar metal hydroxide sludge. The boiler blowdown represents an additional by-product stream for disposal by contract hauling. The safety concerns associated with transportation and disposal of these sludges would be similar for a Zerpol® or conventional system.

From the standpoint of occupational safety, it should be noted that cyanide and acid-bearing streams were not segregated prior to cyanide destruction in the Zerpol® process. All flows were collected in a common tank prior to initiation of treatment. Certain precautions must be recognized to manage intentional or accidental releases of high strength cyanide and acid solutions to prevent creation of a safety hazard in the workplace. Provision of double-walled tanks, alarms, automatic pH monitors, etc., are warranted to minimize risks.

Performance

Attainment of a zero discharge condition represents an absolute limit in performance. Although a residual sludge solids and salts stream is produced, the three facilities have successfully operated in a zero liquid discharge mode for over three years.

The zero discharge condition was not achieved without careful consideration of rinsewater quality requirements. The variation in condensate and treated effluent quality reported in Tables 14-16 and 18 may be a significant concern with respect to maintenance of product quality. Boiler upsets produced a reuse water of unacceptable quality, necessitating an alternate source or positive control of rinsewater make-up by some form of treatment. Even during optimal boiler operating conditions, the condensate would probably be unacceptable for critical rinsing operations in many production facilities. Supplemental treatment of the reuse streams would be necessary in these cases.

One of the major difficulties encountered in chemical treatment of metal finishing wastewaters is process control and stability. The influent wastewater characteristics are often highly variable, with radical changes in composition occurring over periods of minutes. The Pioneer Metal Finishing influent exhibited pronounced changes in composition as evidenced by the grab sample results summarized in Table 17. The batch nature of the treatment operation simplified control of the treatment operation. Provision of flow equalization is commonly practiced to facilitate control of treatment operations.

Required Operator Skill

The three systems were operated by individuals with little or no formal training in chemistry or environmental engineering. The operators all retained original assignments elsewhere in the plant. Based on the preceding information, it might be concluded that operation of the system can be easily and quickly mastered. The converse is likely the case, with specific details that must be identified through operating experience with a particular system.

Based on several years' experience, the operators have learned to identify problems with the reuse water quality on the basis of associated effects on the production activities. This approach depended heavily on local experience rather than science. This approach did not require extensive wastewater analysis for process control.

The chemical doses were not established on the basis of any fundamental theory or detailed evaluation of influent characteristics. Typical testing for process control was limited to measurement of condensate dissolved solids with a conductivity meter, crude jar tests for evaluation of chemical doses, and determination of pH for control of chemical doses. Use of a colorimetric procedure for analysis of cyanide was practiced by Plate-Rite Co. to optimize peroxide doses.

The lack of rigor in selecting initial chemical doses is one luxury associated with any batch process with a long cycle time, including the Zerpol® process. The operator has ample opportunity to adjust doses a second or third time if necessary to obtain satisfactory quality before initiation of the next treatment cycle.

The potential occupational hazards associated with cyanide wastestreams is particularly acute with the Zerpol® process due to the absence of segregation of the cyanide stream. Proper education and training of personnel is necessary to manage the different cyanide and acid-bearing streams to minimize risks.

Degree of Applicability

The batch treatment process would presumably be compatible with any wastestream which could be treated with chemical methods. The potential problems with applicability relate to compatibility of plating and cleaning chemicals with boiler operation. A number of compounds are known to complicate operation of the boiler. It must be conceded that other unknown compounds in present or future use may also cause substantial problems with operation of the boiler.

Many plating operations in the electronics industry are believed to require rinsewaters of greater purity than would be available as condensate or batch treated effluent as characterized by this study. In these cases,

supplemental treatment of the rinsewater source must be practiced to assure satisfactory product quality. Some variability in condensate quality must be expected during periodic boiler upsets. This factor would be of obvious concern to operations with demanding rinsewater specifications.

All of the facilities which were surveyed represent rather small wasteflows, ranging from 2500 to 5000 gallons per day. Other Zerpol® zero liquid discharge systems are presently in operation at facilities with flows as great as 30,000 gallons per day. In general, selection of batch treatment processes is not cost-effective for large applications. A breakpoint for selection of a continuous flow system at a flowrate between 24,000 and 245,000 gallons per day has been reported (4). Actual cost data were not available for Zerpol® systems in this upper flow range for evaluation. In any case, economic factors mandate successful water conservation and flow reduction for any batch method of treatment.

Advantages and Limitations of Process

The obvious advantage of a zero discharge system is compliance with all effluent regulations (including TTO), present and future. Protection of receiving waters and POTW operation is assured in spite of process upsets, accidental releases, or unanticipated variation in influent wastewater composition. Even though a leak in a heating coil resulted in an excessive cyanide concentration in the wastewater at Pioneer Metal Finishing, there was no liquid discharge of cyanide due to this upset condition, although elevated cyanide levels were reported in the sludge and blowdown. This security and stability was cited by the industries as a principal reason for selection of the Zerpol® system.

Because the treatment process is conducted in a batch processing mode, operator attention can be scheduled at a convenient time. This flexibility allowed assignment of existing personnel for operation of the wastewater treatment system without significant interruption of prior duties. This advantage would be shared by all batch processes with comparable cycle times. The manpower commitments were reported to vary from two to five hours per week per shift for the three facilities. Periodic monitoring of

condensate quality must be performed throughout boiler operation to maintain rinsewater source quality.

The extended detention which is available from the large tank volumes affords some flexibility in timing of treatment operations. Each reaction tank is large enough to contain all flows for at least a three-day period. This allows time for adjustment of chemical doses, repair and maintenance of equipment, and consultation and troubleshooting in the event of problems. The extended detention provides the operator with more than one opportunity to identify an optimum chemical dose, thereby avoiding overdoses which might be practiced to be on the safe side if only one attempt were permitted.

Several important constraints were identified which would restrict application of the Zerpol® system. Certain chemicals were not compatible with the boiler. This constraint may require abandonment of these compounds in plating and cleaning solutions. Boiler feed chemicals could conceivably mitigate some of the foaming problem. It should be noted that this restriction may restrict flexibility to adopt new plating or cleaning compounds in future operations. Control of plating and cleaning solutions must be established for successful operation of the wastewater treatment system.

The success of the zero discharge system requires recirculation of treated effluent and condensate as rinsewater make-up. This practice did not impair product quality at the three facilities which were surveyed. Specifications for rinsewater source quality must be evaluated for each individual plating operation. The level of dissolved salts and other impurities in the reuse water streams would not be compatible with many metal finishing activities. In these cases, auxiliary treatment of a continuous make-up water stream may be essential. The variability in condensate quality due to irregular boiler performance would also be a concern for metal finishing operations in which high quality rinsewaters were essential.

Because the process depends on reuse of water to achieve a zero discharge mode of operation, careful attention to a water balance is necessary. Successful operation of the boiler and batch treatment process is imperative to generate the water needed for operation of the metal finishing production lines. A temporary malfunction of the treatment system should not cause an

interruption in production due to the available storage of condensate and treated effluent. A prolonged interruption (exceeding several days) in water supply may have adverse consequences for production.

The economics of the process dictate a substantial reduction in flow. The treatment systems had little flexibility to accommodate flows in excess of design values due to finite tank capacities. A minimum batch cycle time of two days was prudent to allow for proper identification of chemical doses and subsequent solids-liquid separation.

Build-up of salts in the system was also noted to result in difficulties with maintenance of product quality. Consequently, peroxides were used for cyanide oxidation instead of chlorine compounds. Due to the high costs for peroxide, all efforts to reduce cyanide content of the raw wastewater achieved a substantial reduction in treatment costs. Measures to reduce drag-out by addition of counterflow rinses, improved racking or drainage of pieces, or reduction of cyanide bath concentrations was desirable in this regard. Removal of calcium and magnesium from make-up waters was also necessary to maintain boiler function.

SECTION 7

ZERPA - DISTILLATION SOLVENT RECOVERY

PROCESS DESCRIPTION

Distillation of organics is widespread in the chemical production industry for separation of various compounds. Recovery of valuable solvents by distillation is also practiced, however substantial quantities of spent solvent are normally required to justify the expense of development and operation.

Zerpa Industries, Inc. (currently Recyclene Products, Inc.) introduced a small-scale batch distillation unit in 1981 which is covered by U.S. Patent No. 4,457,805. The equipment is marketed for recovery of solvents with a boiling point less than 400°F. The apparatus contains a heating element, condenser, and storage reservoir for recovered solvent. An innovative feature of the process includes recovery of residue from the distillation operation in a nylon or teflon bag. This bag can be simply removed from the boiler in much the same manner as a liner is removed from a garbage can. The residual material remaining after distillation is thus packaged for final disposal.

The process has been installed in a variety of industries for recovery of many solvents of interest to the metal finishing community such as freon, trichloroethylene, 1,1,1, trichloroethane, VM & P naphtha, methyl ethyl ketone, toluene, and lacquer thinner.

The units are marketed with capacities ranging from 14 to 35 gallons per batch. A continuous feed unit with a capacity of 20 gallons per hour has recently been introduced. The limited capacity provides the smaller generators with an economical alternative for solvent recovery, thereby reducing costs for virgin solvent purchase and spent solvent treatment and disposal. All units are rated for National Fire Protection Association

Class I, Division 1, Group D Environment (5). Group D chemicals include acetone, alcohol, ethylene dichloride, lacquer solvent, naphtha, vinyl chloride, and xylenes. Class I, Division 1 locations refer to sites in which the hazard exists or may exist by reason of ignitable concentration of combustible gases or vapors under normal operating conditions or during maintenance and repair operations.

APPLICATION AT W. A. PARSONS COMPANY - DURHAM, CT

The W. A. Parsons Company is engaged in the fabrication of various sheet metal pieces. The operation includes various painting and paint drying processes. A solvent blend was recovered with a 14 gallon Zerpa distillation unit which contained the following components:

1. Toluol - (20%)
2. Butanol - (20%)
3. Ethylene glycol mono ethyl ether acetate (cellosolve acetate) - (15%)
4. VM & P Naphtha - (45%)

Generation rates of spent solvent did not exceed 100 gallons per month.

A closed-loop cooling system was installed to reduce water requirements. Specifications for cooling water for this particular unit required a flow of 20 gallons per hour, maximum temperature of 80°F, and a water pressure of 10 to 110 psi. The power requirements were 110 VAC, 60 Hz at 8 Amps. The unit is illustrated schematically in Figure 8, and has been in operation since May 1983.

The spent solvent was collected in a drum until a sufficient amount was available to warrant operation of the recovery unit. The batch operation included a 12-hour distillation cycle followed by a cooling period of several hours. Turnaround of one batch per day was feasible.

Selected photographs of this Zerpa installation are included in Appendix D.

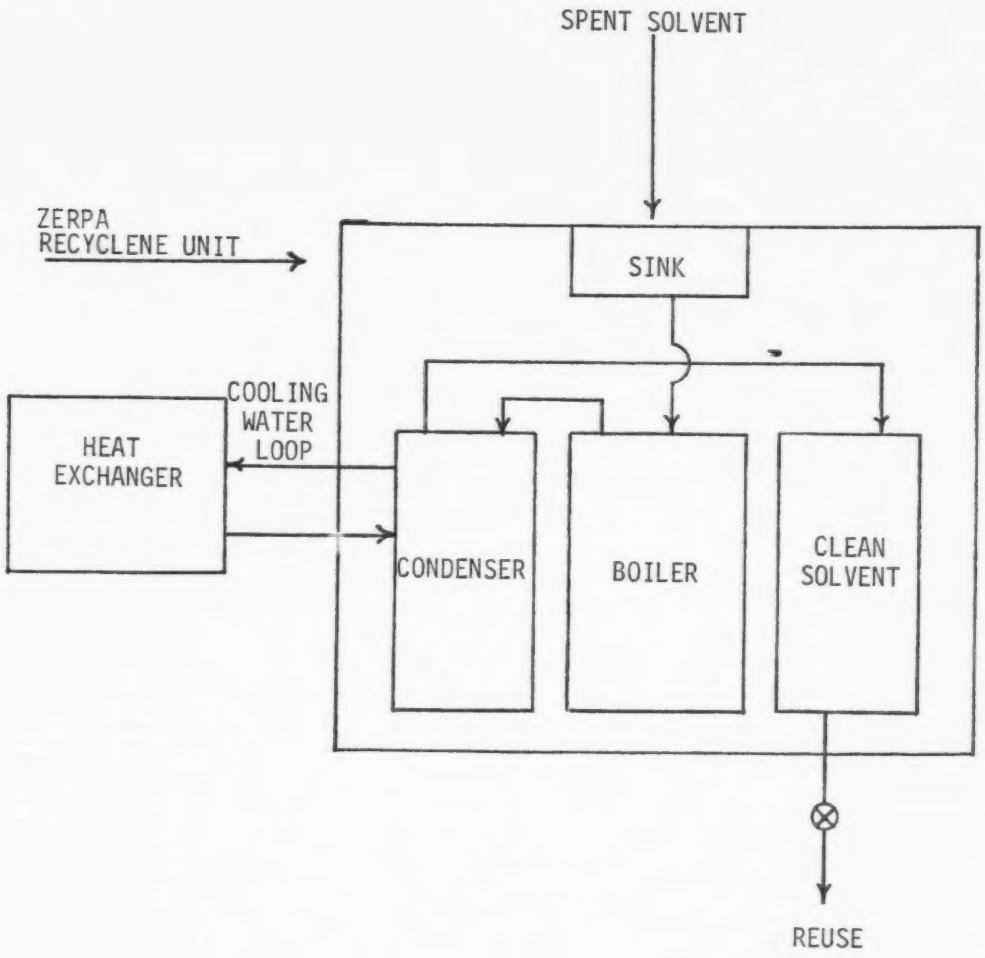

Figure 8. Process flowsheet-distillation solvent recovery.

SAMPLING PROGRAM

Objectives

The objectives of the sampling and analytical program were to characterize the quality of the recovered solvent in comparison to the virgin solvent. Samples were also obtained for spent solvent prior to processing.

Sample Location and Frequency

Samples were collected to correspond with the input and output streams of three separate batch cycles spanning six weeks in the spring of 1984. One virgin solvent sample was also collected.

Analytical Program

The samples were analyzed for the four solvent blend components:

1. Toluol
2. Butanol
3. Cellosolve acetate
4. VM & P Naphtha

Results

A selected summary of the data is presented in Table 20. The reported values represent three batch cycles.

The composition of the recovered solvent generally approximated the composition of the virgin and spent solvents. A nominal systematic increase in the percentage of cellosolve acetate at the expense of toluol and butanol was observed. Representatives of W. A. Parsons Co. indicated that the recovered solvent and virgin solvent yield satisfactory results in production activities, so that the recovered solvent was substituted for virgin solvent without adverse process effects.

TABLE 20. CHARACTERIZATION OF RECOVERED SOLVENT BLEND

	Influent	Effluent	Virgin Solvent
Toluol			
Mean, %	31.0	25.9	20.2
Standard Deviation, %	3.3	3.5	
Maximum, %	34.3	31.0	
Minimum, %	27.0	23.2	
Number of Data Points	5	6	1
Butanol			
Mean, %	14.7	13.3	17.6
Standard Deviation, %	1.3	0.9	
Maximum, %	16.3	15.2	
Minimum, %	13.0	12.8	
Number of Data Points	5	6	1
Cellosolve Acetate			
Mean, %	13.0	21.6	18.1
Standard Deviation, %	5.3	3.1	
Maximum, %	21.8	26.5	
Minimum, %	8.1	17.3	
Number of Data Points	5	6	1
V M & P Naphtha			
Mean, %	41.1	38.3	44.0
Standard Deviation, %	3.9	3.2	
Maximum, %	43.8	42.3	
Minimum, %	34.2	34.8	
Number of Data Points	5	6	1

EVALUATION OF PROCESS

Energy Requirements

Operation of the W. A. Parsons unit for a 12-hour period required 10.6 kwh of electricity (8 amps, 110 volts). A similar energy requirement was necessary for operation of the cooling water recirculation system. The total energy requirement was 21 kwh per batch. This corresponded to 1.8 kwh per gallon, assuming a spent solvent volume of 12 gallons per batch. The unit power cost for W. A. Parsons was $0.087 per kwh, with a corresponding

energy cost of $0.15 per gallon. Similar unit energy requirements would be expected for other capacity systems.

Cost

Capital costs for the various capacity Zerpa units are summarized in Table 21. The cited prices are for the basic unit only with a 1984 cost basis. Additional costs would be required for various options which include water recirculation kits, stainless steel materials for condenser, temperature gauges, flow meter, overheat safety shutdown, and chiller for low boiling point solvents (e.g., Freon).

In addition to electricity, operating expenses at W. A. Parsons were incurred for labor (one manhour per batch), liner consumption (1.5 batches per nylon liner), and sludge disposal. The residual solids represented 10 to 15 percent by volume of the spent solvent. A summary of operating costs is outlined in Table 22. Labor was the greatest cost factor for this small recovery operation.

The economic feasibility of recovery depends heavily on virgin solvent purchase costs and production levels for recovery of capital costs. Payback periods for several applications are reported in Table 23, based on information supplied to Zerpa Industries Inc. by a number of clients. Details regarding the method for calculation of payback period were not supplied. A payback period of slightly more than 24 months was expected by W.A. Parsons.

Safety Considerations

Two concerns are evident from the standpoint of safety. Release of vapors may occur during distillation if there is a failure of the gasket seal. Preventive replacement of the gasket and provision of adequate ventilation should be practiced to minimize the risk of exposure to employees.

Many of the potential solvents are flammable. The Zerpa units are represented as safe for these flammable materials, and the systems are rated for NFPA Class I, Division 1 Group D environment.

The unit at W. A. Parsons was housed in a separate structure which was also used for storage of spent and regenerated solvents. This area was not

TABLE 21. CAPITAL COST ESTIMATES
ZERPA SOLVENT RECOVERY

Model	Capacity Gallons	Purchase Price (1984 $)	Nylon Liner $/Bag	Teflon Liner $/Bag
RS-14A	14	4715	2.37	14.25
RS-20	20	9622	4.71	19.79
RS-35	35	14186	4.71	28.50

TABLE 22. OPERATING COST SUMMARY
ZERPA SOLVENT RECOVERY

	$/Gal
Electricity	0.15
Labor (@ $10 per hour)	0.83
Liners	0.12
Sludge Disposal ($80/Drum)	0.18
	$1.28

TABLE 23. PAYBACK PERIOD
ZERPA SOLVENT RECOVERY INSTALLATIONS

Solvent	Capacity of Unit, Gallons	Payback Period, Months
Methyl ethyl ketone	14	13 to 14
Freon and 1,1,1 Trichloroethane	35	18
Acetone, trichloroethylene, and perchloroethylene	14	< 12
Methylene chloride	14	18

normally occupied by plant personnel, thereby minimizing any risk of chronic exposure to personnel.

Performance

The quality of the reclaimed solvent was satisfactory for use in lieu of virgin solvent at W. A. Parsons Co. Many other installations are successfully reclaiming a variety of solvents.

Required Operator Skill

Very little specialized skill was required for operation of the distillation unit, once an operating temperature and duration were established. Identification of optimum temperatures required a period of several months at W. A. Parsons to become familiar with the capability of the system. Theoretical temperatures based on normal boiling points did not yield the optimum point of operation. A willingness to experiment with system variables to locate the optimum operating point was necessary. W. A. Parsons Co. representatives favored a lower temperature to prolong the life of the nylon liners.

Degree of Applicability

The technology appears to have a great diversity of application, as evidenced by the variety of solvents which are currently recovered with this process. Greater solvent quantities, elevated unit costs for disposal of spent solvent, and increased value of virgin solvents would all tend to favor recovery.

A few technical limitations should be noted. The maximum operating temperature is 390°F, so that recovery of solvents with a greater temperature would not be practical. Addition of a chiller may be necessary to condense compounds with a depressed boiling point.

Advantages and Limitations of Process

The economic features of the Zerpa solvent recovery system are quite attractive in light of the reported payback periods. Another significant advantage of the process is a reduction in hazardous materials for ultimate disposal. Recovery and reuse of these organic compounds is definitely preferable to disposal from the standpoint of environmental contamination and consumption of raw materials.

Some technical complications preclude the use of these systems for applications which would require temperatures greater than 400°F. Separation of compounds with similar boiling points could not be expected in a single-stage system.

Safety considerations may warrant certain precautions with respect to location of a unit. These complications are definitely manageable, however.

Application of a distillation process for recovery of solvents offers economic benefits to the user, particularly with respect to solvent purchase and residual solvent disposal costs. Compliance with TTO effluent limitations depends on efficient separation of solvents from the wastewater effluent. This latter separation operation is not related to operation of the distillation unit, so that development of this type of solvent recovery program does not address the TTO effluent standard.

REFERENCES

1. Federal Register. 40 CFR Parts 413 and 433, 48 (137): 32462-32488.

2. Dietz, J. D. AES and EPA Seek New Treatment/Recovery Techniques. Plating and Surface Finishing, 70 (9): 28, 1983.

3. Militello, P. A. Assessment of Emerging Technologies for Metal Finishing Pollution Control: Three Case Studies. Contract No. 68-03-2907-09, U. S. Environmental Protection Agency, Cincinnati, OH.

4. Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category. EPA 440/1-83/091, U. S. Environmental Protection Agency, Washington, DC, 1983.

5. National Fire Protection Association. Inspection Manual, 4th Edition. Boston, MA, 1976.

6. American Public Health Association. Standard Methods for the Examination of Water and Wastewater, 15th Edition. Washington, DC, 1981.

7. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, U. S. Environmental Protection Agency, Cincinnati, OH, 1979.

8. Test Methods, Technical Additions to Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055, U. S. Environmental Protection Agency, Cincinnati, OH, 1982.

9. American Society for Testing and Materials. Standards on Chromatography, 1st Edition, Philadelphia, PA, 1981.

10. Miller, I. and Freund, J. E. Probability and Statistics for Engineers, 2nd Edition. Prentice Hall Inc., Englewood Cliffs, NJ, 1977.

APPENDIX A

ADVERTISEMENT OF PROJECT

The American Electroplaters' Society, Inc. in cooperation with the Nonferrous Metals and Minerals Branch of the U.S. Environmental Protection Agency wishes to identify and locate new or novel technologies for the treatment of liquid and/or solid wastes generated by the electroplating/metal finishing industry. Particular interest is expressed in pollution control technologies which involve conservation of resources (energy, water, and by-product recovery) as well as effluent treatment. The purpose of this study is to evaluate the effectiveness and potential of the "emerging" technology for applicability on an industry-wide scale. If you are aware of any such technology presently in operation in an electroplating/metal finishing facility, please contact the researcher:

Dr. John D. Dietz
University of Central Florida
P.O. Box 25000
Orlando, FL 32816
(305) 275-2388

APPENDIX B

QUALITY ASSURANCE CONSIDERATIONS

The following material was extracted from the Quality Assurance Project Plan developed prior to initiation of sampling and analytical activities.

QA OBJECTIVES FOR MEASUREMENT DATA

The major measurement parameters and their QA objectives in terms of precision and accuracy are listed in Table B.1. Precision (repeatability) is defined as a measure of mutual agreement among individual measurements of the same property, under prescribed similar conditions. Precision was expressed as a standard deviation--either as a percentage of the measured value or in absolute terms, i.e., mg/L. Accuracy is a measure of "trueness" or "closeness to reality" of the measurements. It is assessed by comparing the measurements with an accepted reference or true value of standards. Accuracy was expressed as a percentage of the true value, 100 percent (X/T), where X is the measured value and T is the true value.

QUALITY CONTROL CHECKS

Replicates

Replicate samples are employed to evaluate the precision associated with reported values of environmental parameters. In this study, the variances could be attributable to three principal error sources: analytical equipment, sampling and analytical procedures, or time-dependent variation in the process water characteristics. It is expected that the latter variance contributed the greatest sources of variation. This error source is referred to as the process variance.

TABLE B.1

PRECISION AND ACCURACY OBJECTIVES

Measurement Parameter	Precision % (or as noted)	Accuracy %
pH	0.1 units	95-105
Total Dissolved Solids	10	90-110
Total Solids	10	90-110
Total Suspended Solids	10	90-110
P	15	80-120
CN	20	80-120
Metals: Ca	15	80-120
Cd	15	80-120
Cr	15	80-120
Cu	15	80-120
Fe	15	80-120
Mg	15	80-120
Ni	15	80-120
Zn	15	80-120

Evaluation of the precision of the analytical test was evaluated by analysis of split samples prepared in the laboratory. A minimum of five replicates were analyzed in this manner to establish the analytical variance. The variance was determined in this manner daily for the metals, and once for the other parameters (except organics). Duplicate analysis (split samples) were completed for 5 percent of all samples.

Spikes

Spikes were prepared by adding sufficient stock solution to the sample to approximately double the concentration of the measured parameter. The calculated concentration of the spiked sample is given by:

$$\text{Conc}_{\text{spike}} = \frac{\text{Conc}_{\text{sample}}\ \text{Vol}_{\text{sample}} + \text{Conc}_{\text{stock}}\ \text{Vol}_{\text{stock}}}{\text{Vol}_{\text{sample}} + \text{Vol}_{\text{stock}}}$$

The measured value of the spike must agree with the calculated value to within the criteria established in the QA objectives for measurement data.

Blanks

Field blanks, created by adding distilled water into a rinsed sampling container, were analyzed for each parameter once for each sample location (except organics). Laboratory distilled water blanks were analyzed as well to check for contamination in sample handling methods after arrival in the laboratory.

Internal Standards

Internal standards are those prepared from stock solutions and were used to periodically check the analytical accuracy of the system. Each time a new internal standard was prepared, it was analyzed a minimum of five times. All measurements must fall within the precision and accuracy limits established for the particular measured parameter. New internal standards were prepared once each month or more frequently as needed.

PERFORMANCE AND SYSTEM AUDITS

A three-phase performance and system audit was conducted as defined by the EPA Quality Assurance Officer and EPA Project Officer. The audit involved analysis of unknown samples supplied by the EPA's Environmental Monitoring and Support Laboratory for parameters applicable to this project (Ca, Mg, Cd, Cr, Cu, Fe, Ni, Zn). The QC samples consisted of:

A. Defined samples for analysis for the purpose of verification of analytical system prior to analysis of project field systems.

B. Performance Evaluation samples provided through EPA's WP012 Study spiked into laboratory pure water.

C. IERL Evaluation samples spiked into specific field samples.

Analysis of organics as a part of any performance audit was not included.

ANALYTICAL PROCEDURES

pH — A Corning Model 120 pH meter was used to measure pH. The electrometric procedure is stated in Section 424 of Standard Methods (6).

TS, TDS, TSS — Solids analyses were determined as prescribed in Section 208A, 208C, and 208D of Standard Methods (6), respectively.

CN — Cyanide was analyzed by Method 335.2 (spectrophotometric) of the EPA Manual, Methods for Chemical Analysis of Water and Wastes (7).

Metals, P — Metals were analyzed following the general procedures stated in EPA 600-14-79-020, Methods for Chemical Analysis of Water and Wastes (7), as modified by EPA 600/4-82-055 (8), Method 200.7, with the exception of instrumentation. The SMI Spectraspan III (DC arc plasma) was used in lieu of the ICP instrument. Phosphorous was also analyzed by DC arc plasma following these procedures.

Organics — The organic constituents (naphtha, butanol, toluol, and ethylene glycol monoethyl ether acetate) were analyzed by gas chromatography by direct injection with flame ionization detection in accordance with ASTM Method D3695 (9).

RESULTS OF QA TESTS

A summary of relevant QA analyses is presented in Tables B.2 - B.6.

In consideration of the collective data, it is apparent that maintenance of satisfactory performance was more difficult at low concentrations. Precision objectives were satisfied in all cases except one low concentration of Cd, Zn, and TDS and two cases for CN. Satisfactory precision was achieved for these tests at higher concentration ranges, with the exception of CN. It appears as though the laboratory performance with respect to cyanide did not consistently satisfy the project objectives.

With respect to accuracy, satisfactory results were obtained for all metals at concentrations in excess of 0.02 mg/L, except iron. Replacement of an electronic component in the iron channel was completed prior to analysis of any field samples to correct the analytical problem.

The concentrations which were encountered in the research program almost universally exceeded 0.02 mg/L, so that the difficulty with achieving the accuracy objective at low concentrations was not a major concern. Metal concentrations were not reported in this research effort to a greater accuracy than 0.01 mg/L, based on a recognition of this analytical limitation.

Some matrix effects were documented based on the analysis of spiked matrix samples reported in Table B.6. Certain restrictions on interpretation of the results are noted on Table B.6.

TABLE B.2

EVALUATION OF PRECISION

Parameter	Mean mg/L	Standard Deviation mg/L	Number of Observations	Precision %
Ca	3.73	0.11	5	2.8
Ca	9.44	0.20	5	2.1
Cd	0.02	< 0.01	5	47.5 (a)
Cd	14.15	0.26	5	1.9
Cr	3.31	0.07	5	2.1
Cr	47.6	0.72	5	1.5
Cr	0.13	0.01	6	9.7
Cr	37.88	0.89	5	2.4
Cu	69.2	1.0	5	1.5
Cu	5.71	0.07	5	1.3
Cu	4.19	0.04	5	1.0
Cu	0.53	0.01	6	2.5
Fe	8.10	0.12	5	1.4
Fe	10.5	0.1	5	0.4
Fe	49.34	1.11	5	2.3
Fe	0.82	0.04	6	4.8
Mg	2.88	0.13	5	4.3
Ni	203	6	3	2.8
Ni	6.83	0.09	5	1.3
Zn	5.33	0.13	5	1.3
Zn	14.96	0.19	5	4.6
Zn	121	1	5	0.6
Zn	2.55	0.44	6	17.6 (a)
CN	24.0	1.5	5	6.1
CN	292	83	5	28.3 (a)
CN	2.54	0.69	5	27.1 (a)
P	12.7	0.6	5	4.6
P	54.6	1.8	5	3.3
P	19.63	0.52	5	2.6
P	4.02	0.23	6	5.7
SS	675	25	5	3.7
TDS	15600	1300	3	8.1
TDS	85	13	3	15.6

(a) Did not satisfy precision objectives.

TABLE B.3

EVALUATION OF ACCURACY INTERNAL STANDARDS

Parameter	True Value mg/L	Reported Value mg/L	Accuracy %
Cd	1.00	1.08	108.0
	2.00	2.17	108.5
	0.100	0.93	93.0
	0.010	0.004	40.0 (a)
	0.010	0.010	100.0
	0.0015	0.003	200.0 (a)
	0.050	0.047	94.0
Cu	1.00	1.13	113.0
	3.00	3.19	106.3
	0.100	0.099	99.0
	0.010	0.009	90.0
	0.040	0.046	115.0
	0.008	0.020	250.0 (a)
	0.250	0.230	92.0
Cr	2.00	2.00	100.0
	6.00	6.18	103.0
	0.100	0.088	88.0
	0.010	0.006	60.0 (a)
	0.060	0.053	88.3
	0.007	0.005	71.4 (a)
	0.150	0.149	99.3
Fe	1.00	1.60	160.0 (a)
	2.00	2.04	102.0
	0.050	0.142	284.0 (a)
	0.017	0.039	229.4 (a)
	0.600	0.350	58.3 (a)
	0.100	0.076	76.0 (a)
Mg	10.00	10.00	100.0
	20.00	19.43	97.2
Ni	2.00	2.07	103.5
	4.00	4.13	103.2
	0.070	0.063	90.0
	0.020	0.015	75.0 (a)
	0.250	0.242	96.8
	0.100	0.096	96.0
	0.010	0.003	30.0 (a)
Zn	1.00	1.08	108.0
	10.00	9.55	95.5
	0.100	0.100	100.0
	0.010	0.003	30.0 (a)
	0.060	0.060	100.0
	0.012	0.017	141.7 (a)
	0.200	0.195	97.5

(a) Did not satisfy accuracy objectives.

TABLE B.4

EVALUATION OF ACCURACY

DISTILLED WATER SPIKES (WP012)

Parameter	True Value mg/L	Reported Value mg/L	Acceptable Range (a) mg/L	Accuracy %
Cu	0.429	0.442	0.368 to 0.485	103.0
Ni	0.711	0.698	0.591 to 0.823	98.2
Zn	0.991	0.980	0.848 to 1.130	98.9
Cr	0.571	0.572	0.407 to 0.709	100.2

(a) Acceptable Range defined as within three standard deviations of true value based on variance reported by study participants.

TABLE B.5

ANALYSIS OF FIELD BLANKS

Parameter	Buoyant Media Filtration	Zerpol®
Zn total, mg/L	< 0.01	< 0.01
Zn soluble, mg/L	0.25	
P total, mg/L	0.06	< 0.01
P soluble, mg/L	< 0.01	
Cu total, mg/L	0.01	< 0.01
Cu soluble, mg/L	< 0.01	
Fe total, mg/L	< 0.01	< 0.01
Fe soluble, mg/L	< 0.01	
Cr total, mg/L	< 0.01	< 0.01
Cr soluble, mg/L	< 0.01	
Ca, mg/L		0.98
Cd, mg/L		< 0.01
Mg, mg/L		0.02
Ni, mg/L		< 0.01
SS, mg/L	< 1	< 1
TDS, mg/L		3.0

TABLE B.6
EVALUATION OF ACCURACY
MATRIX SPIKES - ZERPOL

Matrix	Parameter	True Value mg/L	Reported Value mg/L	Acceptable Range[a] mg/L	Accuracy %
Influent	Cu	0.429	0.441	0.368 to 0.485	102.8
Influent	Ni	0.711	0.678	0.591 to 0.823	95.4
Influent	Zn	0.991	1.075	0.848 to 1.130	108.5
Influent	Cr	0.571	0.611	0.407 to 0.709	107.0
Batch effluent	Cu	0.429	0.442	0.368 to 0.485	103.0
Batch effluent	Ni	0.711	0.698	0.591 to 0.823	98.2
Batch effluent	Zn	0.991	1.129	0.848 to 1.130	113.9
Batch effluent	Cr	0.571	0.756	0.407 to 0.709	132.4[b]
Condensate	Cu	0.429	0.491	0.368 to 0.485	114.5[b]
Condensate	Ni	0.711	0.115	0.591 to 0.823	16.2[c]
Condensate	Zn	0.991	0.656	0.848 to 1.130	66.2[c]
Condensate	Cr	0.571	0.656	0.407 to 0.709	114.8

(a) Acceptable Range Defined as within three standard deviations of true value based on variance reported by study participants.

(b) Although a matrix problem exists, the data support that the technology is working. Since, however, the matrix effect is positive, any decrease to the overall system is assumed to be an artifact of the technology.

(c) The matrix has a negative effect. Reduction is occurring, but the QC data do not support whether or not this reduction is the result of the technology, or the matrix effect, or a combination of the two.

APPENDIX C

STATISTICAL PROCEDURES

A statistical analysis was undertaken to determine the significance of the difference in mean and variance of the reported effluent values for the buoyant media filter and slant-tube clarifier. The procedure was adopted from Miller and Freund (10), involving a t-test for the differences between means and an F-test for the ratio of variances. The results are summarized in Tables C.1 and C.2. The observed differences in mean effluent value were determined to be significant for two parameters, and the observed variances were determined to be significantly different for all but one parameter.

TABLE C.1
EVALUATION OF MEAN EFFLUENT CONCENTRATION

Parameter	Buoyant Media Filter			Clarifier			$t_{Calculated}$	$t_{Tabulated}$
	Mean mg/L	Standard Deviation mg/L	Degrees of Freedom	Mean mg/L	Standard Deviation mg/L	Degrees of Freedom		
Zn[a]	0.79	0.32	21	1.69	1.37	12	2.33	1.69
P	0.87	1.04	21	2.12	2.71	12	1.60	1.69
Cu	0.55	0.42	21	0.51	0.62	12	0.21	1.69
Fe	0.13	0.11	21	0.27	0.34	12	0.44	1.69
Cr[a]	0.03	0.04	19	0.20	0.25	8	2.03	1.70

(a) Difference is significant at 95% level of confidence.

TABLE C.2
EVALUATION OF EFFLUENT CONCENTRATION VARIANCE

Parameter	Buoyant Media Filter		Clarifier		$F_{Calculated}$	$F_{Tabulated}$
	Standard Deviation mg/L	Degrees of Freedom	Standard Deviation mg/L	Degrees of Freedom		
Zn[a]	0.32	21	1.37	12	18.33	2.25
P[a]	1.04	21	2.71	12	6.79	2.25
Cu	0.42	21	0.62	12	2.18	2.25
Fe[a]	0.11	21	0.34	12	9.55	2.25
Cr[a]	0.04	19	0.25	8	39.06	2.48

(a) Difference is significant at 95% level of confidence.

Figure D.1. Main batch treatment storage tanks in foreground with elevated sludge thickening tank mounted on top (Pioneer Metal Finishing).

Figure D.2. Chemical addition slurry tank (Pioneer Metal Finishing).

Figure D.3. Boiler (Pioneer Metal Finishing).

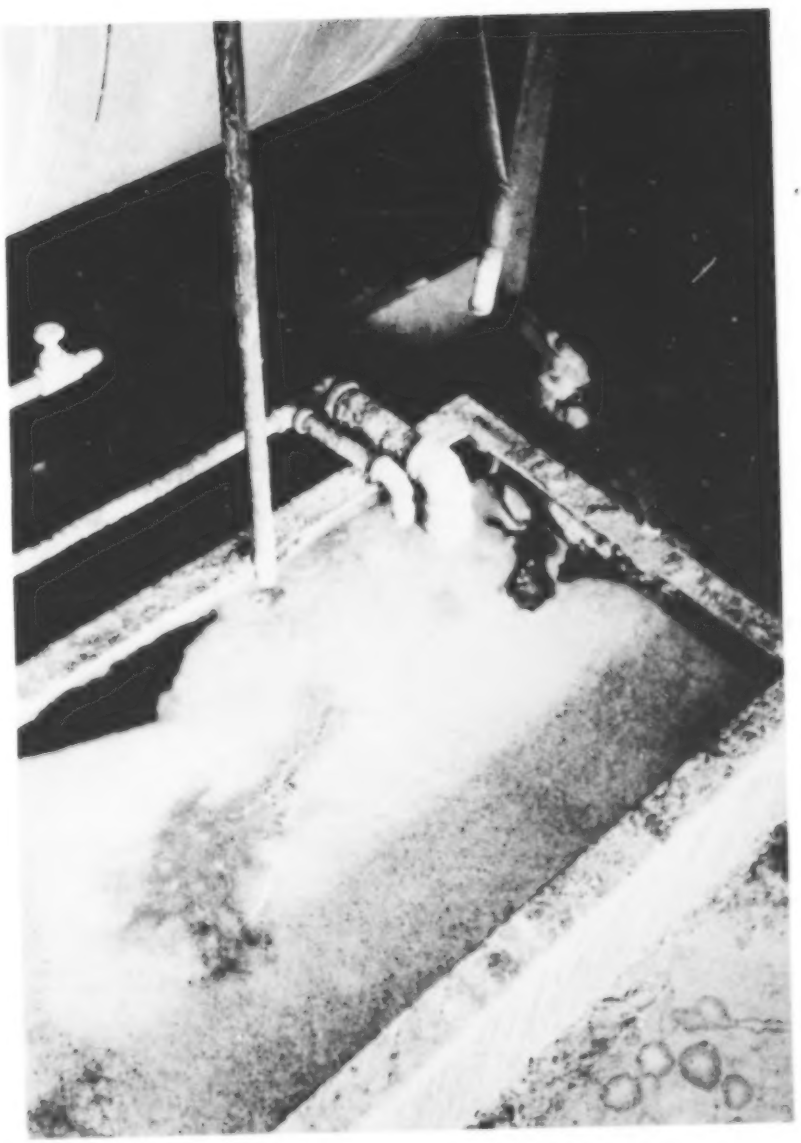

Figure D.4. Boiler blowdown (Pioneer Metal Finishing).

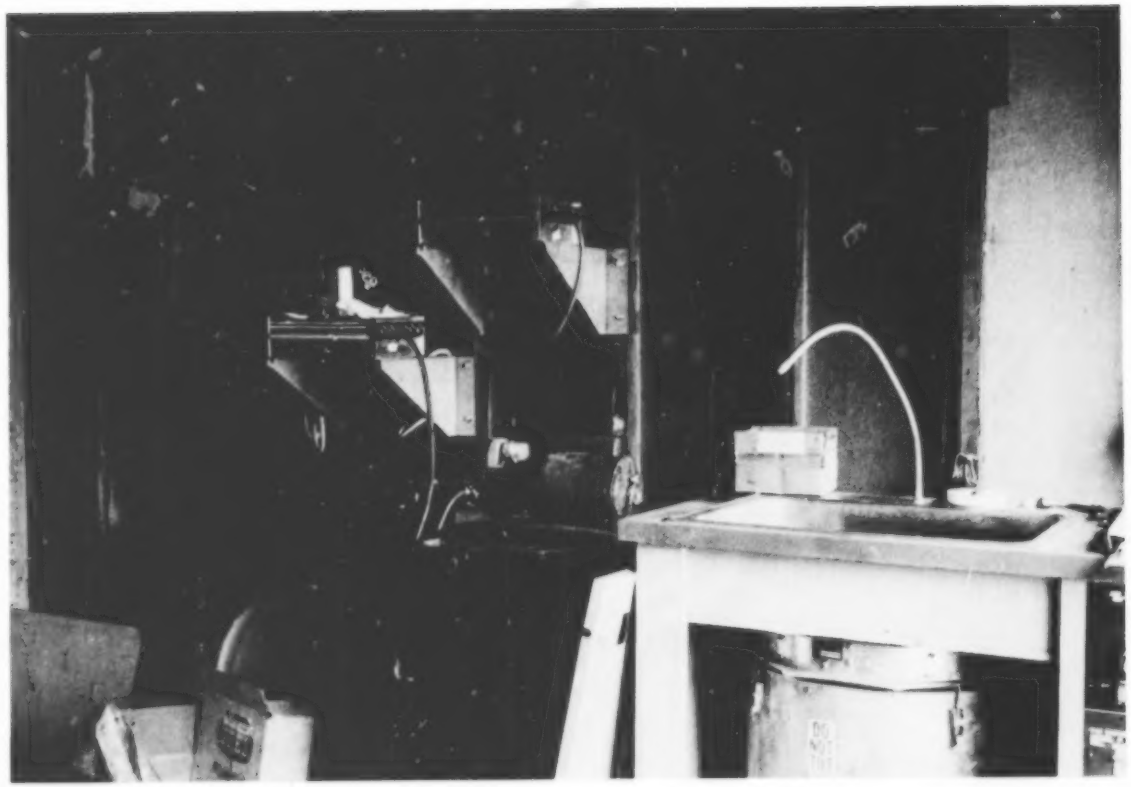

Figure D.5. Zerpa solvent distillation unit with heat exchanger for cooling water source (W. A. Parsons Company).

Figure D.6. Zerpa solvent distillation unit, top view indicating sink for solvent loading (W. A. Parsons Company).

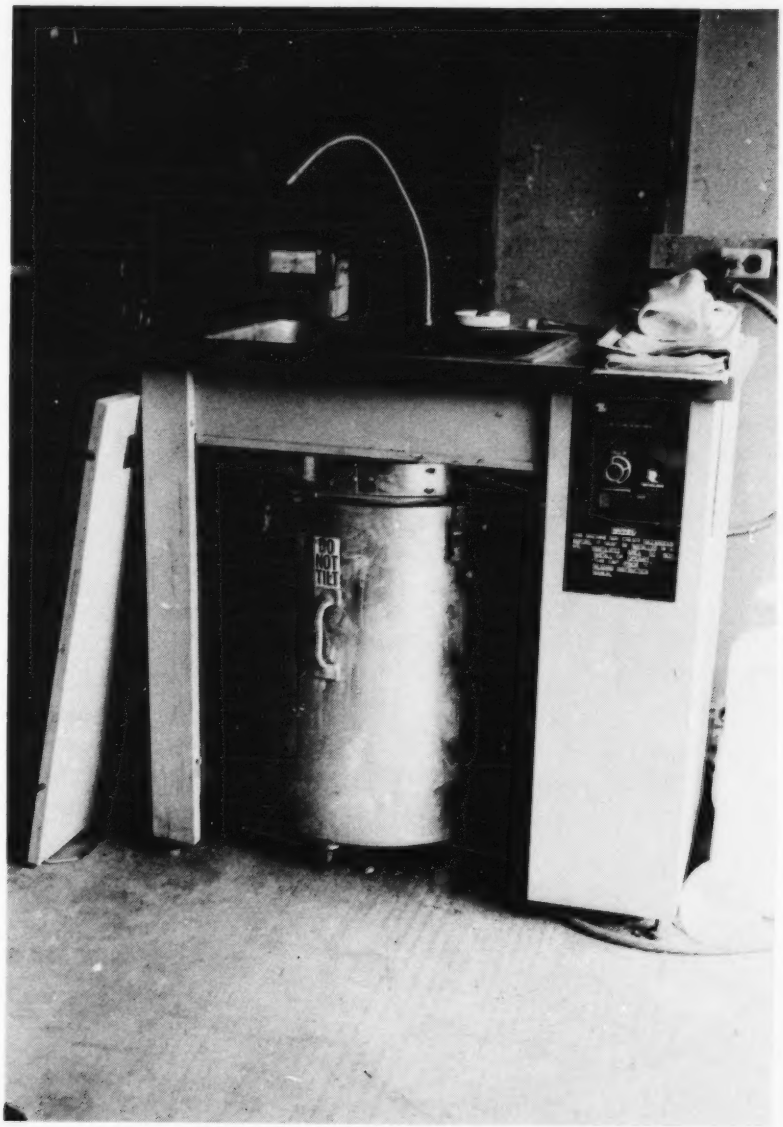

Figure D.7. Zerpa solvent distillation unit (W. A. Parsons Company).

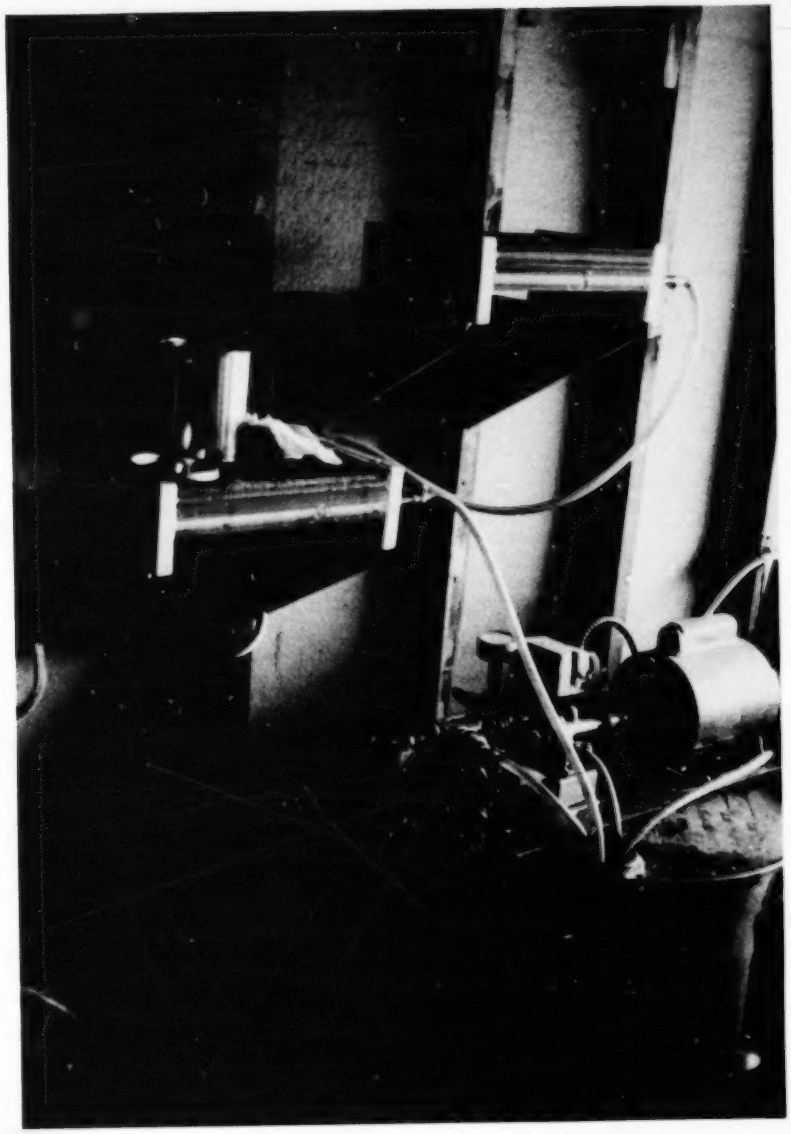

Figure D.8. Heat exchanger for solvent distillation unit (W. A. Parsons Company).